INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.
5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106

CALLAWAY, Bill W., 1944-
HIGH PRESSURE REACTIONS OF SMALL COVALENT MOLECULES.

The University of Oklahoma, Ph.D., 1975
Chemistry, inorganic

Xerox University Microfilms, Ann Arbor, Michigan 48106

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

HIGH PRESSURE REACTIONS OF SMALL COVALENT MOLECULES

A DISSERTATION

SUBMITTED TO THE GRADUATE COLLEGE

in partial fulfilment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By

BILL W. CALLAWAY

Norman Oklahoma

1975

HIGH PRESSURE REACTIONS OF SMALL COVALENT MOLECULES

APPROVED BY

Arnulf P. Hagen

Michael J Pavelich

[illegible] E. [illegible]

Michael R. Abraham

DISSERTATION COMMITTEE

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to his research advisor, Dr. A. P. Hagen, for his support and assistance during this work, as well as for his friendship.

Special thanks go to my friends and family for their encouragement.

Acknowledgement is made to the Oklahoma University Department of Chemistry for teaching assistantships and to the National Science Foundation (GP-19873) for financial support.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

A. Objective

The objective of this research was to investigate the reactions at elevated pressures, between gaseous, relatively inert, covalent compounds. The reactions were selected from those that were known not to take place at atmospheric pressure even at moderately high temperatures, yet these reactions have favorable thermodynamic parameters. Reactions reported in this disseratcaion involve sulfur hexafluoride with CO_2, CS_2 and COS; phosphorus trifluoride with CO_2, CS_2, COS, SO_2, H_2S; and SF_6 with PF_3. It was the purpose of this investigation to determine the following:

1. Was the reaciton favored by elevated pressures up to 4000 atmospheres?

2. What were the minimum conditions of pressure and temperature necessary for reaciton?

3. What was the nature (products, yields, etc.) of these reactions?

4. How did the nature of the products vary with changes in pressure and/or temperature?

5. What possible reaction pathway(s) explain how these reactions proceeded and were effected by high pressures?

B. Effects of Pressure on Chemical Systems

The vast majority of all chemical reactions are observed at one atmosphere or less. Relatively few reaction systems have been investigated at high pressures. Of these reported high pressure reactions, the reactions of organic compounds, usually done in solvents, predominates.[54,119,207] The area of mineral synthesis at extremely high pressures is also a growing area of importance.[42,60] In the field of inorganic chemistry there has been very little reported high pressure chemistry of small molecules.

In a discussion of using high pressure to initiate or facilitate reaction of a system, the questions arise as to how high pressure will affect the thermodynamics and the kinetics of the reaction. Bradley and Munro[26] discuss the effects of high pressure on systems as to how the free energy, ΔG, might be expected to aid the process. It appears that although free energy changes are not negligible, they are small and should not be a major factor in enhancing a chemical reaction at elevated pressures. For gaseous systems, a free energy change of ~ -5 Kcal may be observed for each mole of gas that disappears during the course of a reaction. This effect is realized only by pressures up to 1-2 Kbar. At higher pressures free energy changes are much less per Kbar change in pressure. For condensed phases where the important factor in reactivity is the volume of the transition state, if the volume of the transition state is 10 cm^3/mole less than the volume of the reactants this corresponds to a free energy change of only -0.25 Kcal/mole. The primary factor to be considered in pressure effects on chemical systems appears to be the affect of the change in this transition state volume on the rate constant K according to the equation[119]

$$-\Delta V^* = \frac{\delta(RT\ln K)}{\delta P} \quad (1)$$

Up to pressures of perhaps 1000 atm, the more important effects of pressure on rates takes place by increasing the concentration of the reactants. At pressures greater than 1000 atm other influences on reaction rate become important, factors which effect the rate constant and whose effect might be either to speed up or retard the reaction. From simple collision theory the rate constant K is given by the equation

$$K = PZ \exp(-E/RT) \quad (2)$$

where Z measures the frequency of collisions per unit volume at unit concentration between reacting molecules. P is described as a probability factor or steric factor whose value is usually less than unity and which describes the number of successful collisions that result in a suitable orientation of molecules for reaction to take place. The term E in the exponential is the energy of activation which relates to the number of collisions of the proper orientation that may lead to the transition state and in turn on to products. All three of these terms, P, Z and E may be susceptible to pressure. Since P by its nature is a correction term which is used to explain observed reaction rates where Z and E fail to do so, no general trend of pressure dependance can be formulated. The collision factor Z is not liable to any direct pressure dependence. Some evidence has shown that this factor has the same magnitude for the same reactions in the gas phase as in solution. It would appear that as pressure is increased on a system while more collisions might take place, the problem of diffusion of the molecular species, as the system becomes more viscous, might also restrict the number of these collisions that are suitable for reaction. At a given temperature the exponential term is dependant on the activation energy E which is the energy required to reach the activated complex or transition state which once formed proceeds without further supply of energy to decompose either to products or back to original reactants. Some aspects of the activation energy, that is, in the formation of the transition state are most definitely pressure dependent. Part of the activation energy might be used to force the reacting molecules together more closely. The transition state formed could be associated with a decrease in volume compared to the volume of the unactivated reactants and the energy required to form this transition state could show a strong pressure dependence. The opposite is true of course. If the volume of the transition state for a reaction is greater than the unactivated reactants, then increased pressure would tend to retard the formation of the transition state. A third situation would be one in which there was no volume change between the transition state and reacting molecules. This situation need not be pressure dependant at all unless secondary processes such as electron transfer between reacting species prior to transition state formation be required. Pressure dependence in a system of this sort might very well be observed.

The quantity that leads to an understanding of the effect of pressure on the rate constant K from equation (2) then is the activation volume ΔV^* from equation (1). The activation volume is the difference between the molar volume (more accurately the partial molar volume) of the activated complex and the reactants from which it was derived.[26,119] For gas phase reactions at very low pressures ΔV^* is related in simple fashion to the numbers of molecules involved in the overall stoicicmetry and in the rate limiting step respectively. At higher pressures where gases assume fluid properties like liquids and for condensed phases like liquids and solutions the change in the volume of the transition state is more dependant on the increased density of the system due to solvent inneractions or with the formation or loss of charged particles in the system. Unlike temperature effects which invariably increase chemical rates usually to double the rate constant with each 10° rise in temperature, pressure increases may cause either increases or decreases in the rate constant of from 1/2 to 2 times for every kilobar of pressure rise. Table I shows the relationship between ΔV^* and pressures that tend to either raise or lower the rate of a reaction by a factor of 3.

TABLE I

Change in ΔV^* vs. Pressure

ΔV^* (cm^3/mole) ($\pm$)	Pressure (atm)
5	5800
10	2900
25	1200
40	700

The magnitude of ΔV^* is normally between +25 and -25 cm^3/mole although values of -40 cm^3/mole have been observed for certain reactions like Diels Alder reactions.[54,202]

Le Noble[119] has summarized the principle mechanistic features that are important in estimating ΔV^*. The values listed for ΔV^* are only approximate of course dependant on any given reaction, but these values can lead to reliable predictions of reaction mechanisms. The mechanistic features are listed in Table II and certain aspects of these ΔV^*'s that are pertinant to this research will be discussed in some detail.

(1) Bond Cleavage: Since the process of homolytic bond cleavage would involve the stretching of a covalent bond prior to free radical formation it would appear that the transition state would have a larger volume than the molecule from which it was derived. This ΔV^* of +10 cm^3/mole has been verified in a number of experiments. For the dissociation of N_2O_4 to NO_2 a ΔV^* of about +10 cm^3/mole was observed.[62] A study of perester decomposition by Neuman and Pankratz also yielded values of ΔV^* of this magnitude.[150] The thermal unimolecular decomposition of benzoyl peroxide has an activation volume of about +10 cm^3/mole.[151] In this type of process increased pressure tends to retard the reaction rate.

(2) Bond Deformation: The majority of bond deformation processes involve racemizations where bond stretching or bending short of bond breaking occurs. ΔV^* varies from -1 to +2 cm^3/mole depending on solvent employed hence the contribution to ΔV^* from the actual racemization of some optically active biphenyls in H_2O were found to racemize a little more slowly at high pressures than at low pressures with ΔV^* about +2 cm^3/mole.[129] The racemization of a number of other enantiomers has also been reported.[131]

(3) Bond Formation: For those types of reactions where two neutral molecules or radicals react to form one, the ΔV^* would by expected to be negative and significant. The Diels - Alder reaction is one of these. Polymerizations also fall into this catagory. It would appear that reactions involving a possible Lewis acid-base molecular adduct

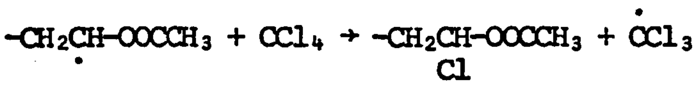
TABLE II

Factors in the Estimation of ΔV_0^*

Mechanistic Feature	Contribution, ΔV^* (cm^3/mole)
Bond Cleavage	+10
Bond Deformation	∿ 0
Bond Formation	−10
Displacement	− 5
Diffusion Control	>+20
Cyclization	0
Ionization	−20
Steric Hindrance	− 0
Neutralization	+20
Charge Dispersal	+ 5
Charge Concentration	− 5

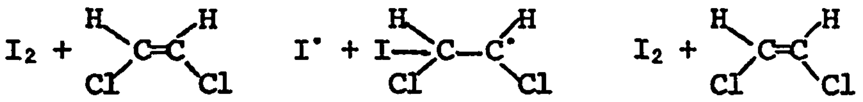
as an intermediate could also be assumed to be pressure favored by this mechanistic feature.

(4) Displacement Reactions: Free radical chain transfer is an example of simulataneous bond cleavage and bond formation between neutral molecules and radicals. The telomerization of vinyl acetate with CCl_4 has been reported to have a ΔV^* of -4 $cm^3/mole^{214}$ for the reaction



$$-CH_2\underset{\bullet}{C}H\text{-}OOCCH_3 + CCl_4 \rightarrow -CH_2\underset{Cl}{C}H\text{-}OOCCH_3 + \overset{\bullet}{C}Cl_3 \qquad (3)$$

Iodine abstraction is probably involved in the iodine - catalyzed equilibration of cis and trans 1,2 dichloroethane by the equation



(4)

This reaction is dependant on the equilibrium

$$I_2 \longrightarrow 2I^{\bullet} \qquad (5)$$

and the activation volume should be slightly positive since the I-I bond cleavage would only be partially compensated by the C-I bond formation. For polar additions the ΔV^* values are reported to be much larger (as much as -10 $cm^3/mole$).

(5) Diffusion Control: At extremely high pressures, 20 to 40 K.bar, the pressure effect has been to retard certain reactions due to the highly viscous, glassy character of certain solvents where the diffusion of the reacting species is slower than the rate determining step resulting in large positive values of ΔV^* ($> +20$ $cm^3/mole$). Hamann has shown that the displacement of bromide from ethylbromide by eugenoxide in a eugenol - isopropanol mixture which was usually accelerated by pressure, as SN2 displacements normally are, was retarded above

20 Kbar.[89]

(6) Cyclization: The direct relationship between ΔV* and the formation of cycles is somewhat confusing since a wide variety of both positive and negative values have been reported. Examples like the Claisen and Cope rearrangements invariably give ΔV* values of about -10 cm^3/mole.[201] For the cyclization of small chain olefins to aliphatic rings ΔV* appears to be about +1 to +13 cm^3/mole probably due to the fact that the cycles formed can not intertwine as the linear olefins can with the center of the rings being dead space and inaccessible to other molecules.[118] Le Noble assigns the ΔV* to cyclization alone as ∿ 0 cm^3/mole and states that other effects like bond breaking and making give rise to the observed values.

(7) Ionization: Ionization is one of the most important features for evaluating the high pressure effects on chemical systems. It would appear at first that since the formation of ions is a heterolytic bond breaking process that the ΔV* might be positive and not favored by increased pressure. The simutaneous formation of a pair of charges alters the picture completely. Whalley[207] in a recent review poses the hypothetical reaction of

$$2Ar \rightarrow K^+ + Cl^- \qquad (6)$$

in which a single charge is transferred between two argon nuclei. Using crystal radii of 1.918, 1.33 and 1.81 Å respectively for Ar, K^+ and Cl^- this reaction would give a ΔV* in the solid state of -15.0 cm^3/mole. The radii in aqueous solution are similar to those in the crystal so the estimation has been made to include solvent effects that the ΔV* of the ions themselves of -21 cm^3/mole.

The formation of ions then either with or without solvent leads to a negative ΔV^*. In solvents the charged ions exert a powerful attractive force on nearby polar or polarizable solvent molecules so that the density of the immediate neighborhood of ions is higher than for the bulk solvent. This volume decrease on ionization is referred to as electrostriction.[50] For weak acids the ΔV^* is always negative and on the order of about -15 cm^3/mole.[88,97] Exceptions to this have been found for carbonic acid[57] ($\Delta V^* = -27$ cm^3/mole) and sulfurous acid[58] ($\Delta V^* = -20$ cm^3/mole). It seems likely that these acids involve two equilibria both of which involve volume decreases: hydration as well as ionization

$$H_2O + CO_2 \rightarrow H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^- \qquad (7)$$

The ionization volume for 15 bases in H_2O has been reported to be on the average about -26 cm^3/mole,[88,97] a striking difference from the acids studied.

Two neutral species can react to form both ionic and covalent products, or to form an ionic product product like an ammonium salt. In either case the ΔV^* tends to be negative and the process is pressure favored.

(8) Steric Hindrance: Some evidence indicates that pressure can overcome steric hindrance at reaction sites. The argument presented by Gonikberg et. al.[71] is that "if in a given transition state the reaction sites have been able to get together only at the cost of interpenetration of several interfering groups, its molar volume will be smaller than it would otherwise be, and such reactions are of course accelerated more (or retarded less) than unhindered reactions." Weale[81] has argued that the steric factor may be due to increased solvation rather than interpenetration of reacting molecules.

(9) Neutralization: Neutralization reactions are affected in a manner just opposite to ionization reactions. The ΔV* of the transition state might be +20 cm^3/mole, but since ions are present in the products, the net change between reactants and products is usually about +5 cm^3/mole.

(10) Charge Dispersal: In the formation of very large ions where the charge is spread over many atoms, ΔV* is usually about +5 cm^3/mole. Here the bond breaking process is more important than the solvation of the ion, electrostriction, which occurs to much less extent for this type of ion.

(11) Charge Concentration: If a large ion breaks to yield a smaller ion and a neutral particle, the degree of electrostriction increases markedly so that the ΔV* will usually be about -5 cm^3/mole.

Besides these previous arguments, other workers have presented discussions on the kinetic effects of high pressure as well as many examples of reaction systems.[87,186]

C. High Pressure Inorganic Chemistry

As Whalley[207] stated in a high pressure review recently the use of high pressure should open up new areas of synthesis in inorganic chemistry. This is indeed a relatively open field where little work has been reported with small covalent molecules.

The polymerization of organo silicon compounds like $(C_2H_5)_3SiCH{=}CH_2$ at pressures up to 5500 atm has been reported.[170] The synthesis of diborane[109] was reported with Pd catalyst present at 150 atm by the reaction

$$2(CH_3)_3B + 6H_2 \rightarrow B_2H_6 + 6CH_4 \qquad (8)$$

The high pressure synthesis of silane[45] also has been reported using an Al/$AlCl_3$ catalyst at 400 atm by the reaction

$$SiO_2 + 2H_2 \rightarrow SiH_4 \qquad (9)$$

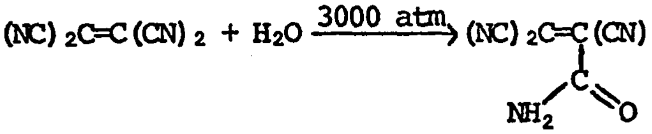
An unusual synthesis of $ClSF_5$[144] has been reported by a two step process, the first step of which is done at 100 atm.

$$CsF_{(s)} + SF_{4(g)} \xrightarrow{100\ atm} CsSF_{5(s)} \qquad (10)$$

$$CsSF_{5(s)} + Cl_{2(g)} \rightarrow CsCl_{(s)} + ClSF_{5(g)} \qquad (11)$$

The hydrolysis to tetracyano ethylene has been reported both at low and high pressures to proceed to different products.[172]

$$(NC)_2C{=}C(CN)_2 + H_2O \xrightarrow[pressure]{no} (NC)_2C{=}C(CN)(OH) + HCN \qquad (12)$$



$$(NC)_2C{=}C(CN)_2 + H_2O \xrightarrow{3000\ atm} (NC)_2C{=}C(CN)(CONH_2) \qquad (13)$$

Exchange reactions with SiF_4 have been reported by Moscony[140] at 3000 atm like

$$[(CH_3)_3Si]_2O + SiF_4 \rightarrow (CH_3)_3Si{-}O{-}SiF_3 + (CH_3)_3SiF \qquad (14)$$

Also reported is the reaction of SiF_4 and SiO_2 at 170 atm to give $(SiF_3)_2O$.

The high pressure hydrolysis of CCl_4 and a series of freons has been reported by Elphingstone and Hagen[83] at 300° and 4000 atm.

Besides these high pressure reactions, others are mentioned in later sections of this introduction in the sections on PF_3, OPF_3, SPF_3 and SF_6.

D. Chemistry of Phosphorus Trifluoride.

Phosphorus trifluoride is a relatively stable compound and even though it was first prepared in 1884,[133] the chemistry of PF_3 is limited.

The hydrolysis of PF_3 has been studied[132,133,137] and the ultimate hydrolysis occurs according to the reaction

$$PF_3 + 3H_2O \rightarrow H_3PO_3 + HF \tag{15}$$

This hydrolysis occurs very slowly[132,133] but occurs rapidly in base. A suggested intermediate formed in this hydrolysis was $HF{\cdot}PF_3$.[132] Phosphorus trifluoride has been reported by Moissan to react with ethyl alcohol but the products were not identified.[133] Phosphorus trifluoride has been reacted with a number of metals and nonmetals at high temperatures with mixtures of fluorides and phosphides as products.[73,74,75] For example

$$6Ni + 2PF_3 \rightarrow Ni_3P_2 + 3NiF_2\ \text{[74]} \tag{16}$$

and

$$6Si + 4PF_3 \rightarrow Si_3P_4 + 3SiF_4\ \text{[132]} \tag{17}$$

Other elements reported to react with PF_3 are Fe, Co, Ca and Na and B. The reaction of PF_3 with halogens also are reported.[133,135,143,209] Phosphorus trifluoride reacts with Cl_2 viz.

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2 \tag{18}$$

This reaction more recently was reported to be catalized by ultraviolet light at room temperature. The product PF_3Cl_2 was reported to attack glass at room temperature.[209] Bromine reacts with PF_3 to give the similar compound PF_3Br_2 which rearranges to give PF_5 and PBr_5.[133] When PF_3 was reacted with I_2 at 300-400° the resulting product, which was a yellow solid when warm but red when cold, was reported to attack glass.[135] The disproportionation of PF_3 was initiated by an electric spark according to the equation

$$5PF_3 \rightleftarrows 3PF_5 + 2P\ \text{[134]} \tag{19}$$

Phosphorus trilfuoride reacted with O_2 in the presence of an electric spark to give OPF_3 as the product. The ΔH for this reaction was reported to be -71 Kcal/mole PF_3.[52] Other workers have studied the reaction of

PF_3 and O_2 in an electric discharge and observed a complicated mixture of OPF_3, PF_5, $P_2O_3F_4$, P_2O_5 as well as polymeric $(PO_2F)_n$.[203] Phosphorus trifluoride is generally thought not to react with glass but at elevated temperatures a reaction has been observed.[19,209] The postulated reaction is

$$4PF_3 + 3SiO_2 \rightarrow 2P_2O_3 + 3SiF_4 \qquad (20)$$

The glass vessel was etched and some P_4 was also observed in this reaction. The reaction of PF_3 and NH_3 in the gas phase has been done with the formation of a white H_2O soluble product,[111] probably NH_4F, among the products. Phosphorus trifluoride has been reported to react explosively with SF_5OF at room temperature to form SOF_4 and PF_5.[195] It was noted that the PF_5 reacted with the glass reaction vessel to form OPF_3. An interesting part of the chemistry of PF_3 is its ability to act as both a Lewis acid or base in forming coordination complexes. Phosphorus pentafluoride, which is a strong electron pair acceptor has been compared in a paper to PF_3, which is a very weak acceptor[143] and the structures of these adducts has been described. Phosphorus pentafluoride readily forms complexes with amines, ethers and nitriles but PF_3 doesn't complex with any of these. Phosphorus trifluoride does not react with KF in vacuo at 240°; however at 150° and 1 atm, PF_3 reacted with KF and CsF[212] viz.

$$3MF + 5PF_3 \rightarrow 3MPF_6 + 2P \qquad (21)$$

It was reported that this reaction might involve an MPF_4 intermediate. Phosphorus trifluoride has been reported to form a weak adduct with $(CH_3)_3N$ that is stable at -78°.[76,77,101] The 1:1 adduct dissociates onwarming to room temperature. Another interesting reaction of PF_3 as a Lewis acid has been postulated in a reaction reported between PF_3 and liquid H_2S.[44] The reaction is postulated to occur by

$$PF_3 + HS^- \rightarrow PF_3 \cdot SH^- \rightarrow HPSF_3^- \qquad (22)$$

Phosphorus trifluoride has been reported to form a very weak adduct at low temperature with SO_3.[213] This also was not stable at room temperature. As a Lewis base, PF_3 is also considered as a weak electron pair donar. Different workers have shown that PF_3 does not complex or adduct with BF_3.[5,6] Phosphorus trifluoride does act as a Lewis base in forming a 1:1 adduct with $AlCl_3$.[6] Another adduct of PF_3 has been reported with B_2H_6 in which $F_3P \cdot BH_3$ is formed under pressure of 8 atm.[162,163] The adduct $BH_3 \cdot PF_3$ has also been prepared at 500°K at a pressure of 6 torr by the reaction of B_2H_6 and PF_3.[64] Phosphorus trifluoride and $B_3O_3H_3$ were also found to form $BH_3 \cdot PF_3$ by the reaction[12]

$$PF_3 + B_3O_3H_3 \rightarrow BH_3 \cdot PF_3 + B_2O_3 \qquad (23)$$

This adduct of $PF_3 \cdot BH_3$ was found to react with O_2 to give gaseous $B_2O_3H_2$. Exchange and substitution reactions of this adduct with mono, di and tri methyl amine have been reported[110,162] with some very interesting results. Trimethyl amine and $(CH_3)_2NH$ both displace the PF_3 from the adduct forming $(CH_3)_3N \cdot BH_3$ and $(CH_3)_3NH \cdot BH$ respectively. Methyl amine however was found to give substitution products like $(CH_3NH)_xF_yP{:}BH_3$ ($x = 1, 2, 3$, when $y = 3, 2, 1$). This reaction was dependant on the amount of CH_3NH_2 employed and no $CH_3NH_2 \cdot BH_3$ was observed. The other product of this reaction was always CH_3NH_2F. The weak base properties of PF_3 were recently demonstated by the reported reaction of PF_3 with mercurous ion in liquid SO_2 to form the $[Hg_2PF_3]^{+2}$ complex ion.[46] This complex ion is unstable and decomposes with warming or exposure to air.

The reactions of transition metal oxides with PF_3 have shown some interesting properties of PF_3 both as a Lewis base as well as a reducing agent.[82] The reactions were carried out at a pressure of 4000 atm and 300°. Nickel oxide reacted with PF_3 to give OPF_3 and $Ni(PF_3)_4$ as products. In addition MoO_3 and WO_3 reacted with PF_3 in the presence of Mg to give OPF_3 and $Mo(PF_3)_4$ and $W(PF_3)_6$ respectively. These reactions did not occur at all at 1 atm. Phosphorus trifluoride shows its base character in exchange reactions where it displaces other electron donars. The reaction

$$Ni(CO)_4 + 4PF_3 \rightarrow Ni(PF_3)_4 + 4CO \qquad (24)$$

has been reported.[16] Other complexes of transition metals have been obtained, viz.

$$M(C_6H_6)_2 + 6PF_3 \rightarrow M(PF_3)_6 + 2C_6H_6{}^{114} \qquad (M = Cr, Mo, W) \qquad (25)$$

The metals Ni, Pd and Pt have been found to react directly with PF_3 to form the corresponding $M(PF_3)_4$ complexes.[115] Some interesting high pressure reactions with PF_3 have recently been reported.[81] Oxygen, S and Se were found to react with PF_3 at 4000 atm and 300° to give OPF_3, SPF_3 and $SePF_3$ with yields of 86% - 96% for OPF_3 and SPF_3 and a yield of 50% for $SePF_3$.

No previous reports describe any attempt of the reaction of PF_3 with CO_2, COS or CS_2 at any temperature or pressure. The reactions of PF_3 with SO_2 or H_2S have not been studied at high pressure, however the high temperature reaction of PF_3 with SO_2 reports free sulfur as one product with trace amounts of SPF_3 and $[F_2(S)P]_2O$ detected as gaseous products.[41] No reaction between PF_3 and SF_6 has been reported.

E. Chemistry of Sulfur Hexafluoride.

Due to the relative thermal stability and inert character of SF_6, few reactions have been reported to date. The reaction of SF_6 and liquid NH_3 has been reported to occur at -64° but the products were not identified.[49] These same workers also report the reaction of Na dissolved in diphenyl - ethylene glycol dimethyl ether with SF_6 at -64° to react giving Na_2S and NaF as products. The room temperature reaction of SF_6 with HI was previously reported.[161] However, later reports showed this reaction to be erroneous.[36] The reaction of Na with SF_6 was done at 250° resulting in the formation of NaF plus other unidentified products.[45] At 200° SF_6 was found to react with $AlCl_3$ to give a mixture of sulfur chlorides and at 250° SF_6 reacted with SO_3 to give SO_2F_2 with a 20% conversion of the SF_6.[35] Sulfur hexafluoride reacts with O_2[180,181] and exploding metals like Al according to the equation

$$3SF_6 + 2Al \rightarrow 3SF_4 + 2AlF_3 \qquad (26)$$

A number of metals and metal oxides have been found to react with SF_6 at temperatures from 500° to 700° to form fluorides and sulfides. None were reported to react below 500°. Higher temperatures yielded only fluorides.[157,158] In a recent high pressure study MgO, SiO_2, NiO and H_2O were found to react with SF_6.[85] The reactions were investigated over a pressure range of 1 - 4000 atm and a temperature range of 25° - 500°. The products in each case were SO_2F_2 and the appropriate fluoride. The minimum reaction conditions were reported to be 475° and 135 atm, with about 10% consumption of SF_6 in each case. At conditions of 500° and 3300 - 4000 atm, as much as 90% conversion of SF_6 was reported. Sulfur hexafluoride also has been reported to react with $LiAlH_4$ in ether producing H_2S in a 10 - 30% yield when reacted for 4 - 7 days.[160] High temperature studies have shown that SF_6 dissociates principally into SF_4 at temperatures up to 1500°K but no lower limits were given in the paper.[210] From 500° to 1000°C the reaction

$$3SF_4 \rightarrow 2SF_6 + S \qquad (27)$$

was studied with less than 1% conversion to SF_6 over this temperature range.[189] It seems likely that at 500°C very little SF_6 dissociates to SF_4 since the presence of large quantities of SF_4 would be present at equilibrium. Sulfur hexafluoride has not been reported to react with CS_2, CO_2, COS or PF_3 either at low or high pressures. Sulfur hexafluoride has been reported to react with Cl_2 in liquid Li at 800° to form salts.[168] A high temperature mass spectroscopy study of the reaction of SF_6 with carbon in a Knudson cell reported the formation of the new molecular species SF, SF_2 and SCF_2.[99]

F. Chemistry of Perfluoromethyl Sulfides.

Bisperfluoromethyl disulfide was orignally prepared in large yields by the reaction of ClF_3 and S[27] probably formed by a free radical mechanism with the generation of the $CF_3S\cdot$ radical. Bisperfluoromethyl disulfide was also prepared in 80% yield by the reacion of IF_5 with CS_2 at 170° for 27 hours.[94] At 200° CS_2 and SF_4 reacted in the presence of catalytic amounts of AsF_3 or BF_3 to give $(CF_3)_2S_2$.[90] It was found that CS_2 reacted with UF_6[198] at 25° to give $(CF_3)_2S_2$. The disulfide has been shown to have a linear structure from both chemical[27] as well as spectral[28] analysis. Bisperfluoromethyl disulfide was not affected by H_2O or $HCl_{(aq)}$ at room temperature but was rapidly hydrolized by aqueous sodium hydroxide to sodium fluoride, carbonate, sulfide and polysulfides.[117] No reaction was noted between $(CF_3)_2S_2$ and H_2 at 300° with Raney Nickel catalyst. The reaction of $(CF_3)_2S_2$ with CoF_3 gave $CF_3\cdot SF_5$ as one product. The disulfide was stable to Cl_2 up to 120° but at higher temperatures, sulfur chlorides and CF_3Cl were formed.

Bisperfluoromethyl disulfide gives a good yield of $Hg(SCF_3)_2$ when reacted with Hg in ultraviolet light. In the absence of Hg the $(CF_3)_2S_2$ gives $(CF_3)_2S$ and S when irradiated with the ultraviolet light.[47,27] An interesting reaction of $(CF_3)_2S_2$ is the telomerization with olefins of the type $F_2C{=}CFX$ ($X = Cl, F, CF_3$). The reaction

$$(CF_3)_2S_2 + nF_2C{=}CFX \xrightarrow[270°]{h\nu} CF_3S(CF_2CFX)_nSCF_3 \qquad (28)$$

gives mostly telomers of n = 1 and 2.[47] By increasing the olefin input polymers of as high as n = 36 have been obtained.[47]

The monosulfide, $(CF_3)_2S$, was first reported as a product of the irradiation of the disulfide.[27] It also is formed by thermally decomposing $(CF_3)_2S_2$ at 320°.[95] Bisperfluoromethyl monosulfide has been prepared by the fluorination of $CS_2 + HgF_2$ at 35°.[126] The structure of the monosulfide is reported by various workers.[125,28] Bisperfluoromethyl monosulfide was thermally decomposed at ambient pressure at 450° to give CF_4, C_2F_6, CS_2 and carbonaceous solids as products. Between 420° - 450° NO_2 reacted with $(CF_3)_2S$ to give CF_4, SO_2 and COS. Above 450° carbonaceous solids were also formed in the NO_2 - $(CF_3)_2S$ reaction.[117] AgF_2 reacted with $(CF_3)_2S$ at 150 - 225° to give CF_4 and CF_3SF_5. CoF_3 reacted with $(CF_3)_2S$ at 175° to give SF_6, CF_4 and CF_3SF_5.[117] Bisperfluoromethyl monosulfide has been reported as being quite resistant to direct oxidation (reaction with O_2).[175] The sulfoxide $(CF_3)_2SO$ has been prepared by the two step process

$$(CF_3)_2S + F_2 \xrightarrow[C_2F_6]{-78} (CF_3)_2SF_2 \xrightarrow{H_2O} (CF_3)_2SO + 2HF \qquad (29)$$

G. Phosphoryl and Thiophosphoryl Fluorides

Phosphoryl fluoride, OPF_3, and its sulfur analog thiophosphoryl fluoride, SPF_3, have been prepared by a number of methods, the most pertinant of which are reported here. The reaction chemistries of

OPF_3 and SPF_3 are quite limited as only a few reactions have been reported.

Phosphoryl fluoride was first mentioned as a product in the reaction of metal fluorides with P_4O_{10}.[178] It was originally prepared by the fluorination of $OPCl_3$ by a variety of fluorination agents like PbF_2[78] and ZnF_2[138]. More recently, other fluorination agents have been used in the preparation of OPF_3 from $OPCl_3$. Antimony trifluoride[22] has been used to prepare OPF_3 in good yields. Calcium fluoride was reported to give OPF_3 in a 90% yield when reacted at 200°.[20] The reaction of PF_3 with O_2 on a platinum sponge at elevated temperatures gave a good yield of OPF_3 plus other products.[136] Phosphoryl fluoride has been prepared from P_4O_{10} with a variety of reagents. Iodine pentafluoride reacted with P_4O_{10} to form OPF_3 which forms a weak complex with the IF_5 in solution.[11] A flow system was used to prepare OPF_3 from P_4O_{10} and SF_4 at high temperatures.[159] Calcium fluoride and P_4O_{10} reacted at 500° to give OPF_3.[194] These same workers also used NaCl to catalize the previous reaction. High pressure, 4000 atm, was employed to prepare OPF_3 from P_4O_{10} and PF_3 at 250°.[86] A synthesis of OPF_3 in high yields and purity was recently reported using PF_5 and O_2 as starting materials in the presence of Mg.[84] Phosphoryl fluoride has been reported to be a product of the incomplete hydrolysis of PF_3Cl_2[185] by the equation

$$PF_3Cl_2 + H_2O \rightarrow OPF_3 + 2HCl \qquad (30)$$

Phosphoryl fluoride has been reported to form a weak adduct with BF_3 which shows that it has some donar properties.[23] A reaction with CsF also was reported <u>viz</u>.

$$2CsF + 2OPF_3 \rightarrow CsPF_2O_2 + CsPF_6 \qquad (31)$$
[123]

The preparations of SPF_3 have been in general similar to those of OPF_3.

Thiophosphoryl fluoride was first prepared by the standard fluorination technique reacting $SPCl_3$ with AsF_3 at 150°.[197] Thiophosphoryl fluoride was reported to be flammable in air unlike OPF_3. At 300° SPF_3 decomposed to S and PF_3.[197] It was also found to react with NH_3 according to the equation

$$SPF_3 + 2NH_3 \rightarrow SPF(NH_2)_2 + 2HF^{197} \qquad (32)$$

SPF_3 has been prepared by the exchange reaction

$$PF_3Cl_2 + S \rightarrow SPF_3 + Cl_2^{171} \qquad (33)$$

Fluorinating agents have been employed in an analogous manner to OPF_3 to make SPF_3. Both PbF_2 and BiF_3 were reacted with P_4S_{10} to form SPF_3.[211] $SPCl_3$ was fluorinated with SbF_3 at pressures greater than 1 atm to give SPF_3.[22]

Antimony trifluoride does not form an adduct with BF_3.[197] It does react with dimethyl amine to give a complex mixture, one product of which was $SPF_2[N(CH_3)_2]$.[38]

H. Chemistry of Carbon Oxides and Sulfides

The reaction chemistries of carbon dioxide, carbon disulfide and carbonyl sulfide reported in the literature are vast and only a part of the previously reported work will be presented in this section. The inneractions of these substances with each other and other pertinant reactions of these compounds with inorganic substances related to those in the dissertation will be reviewed.

1. Carbon Dioxide: Carbon dioxide is quite thermally stable and has been found to begin decomposition in a shock wave apparatus at pressures up to 1000 atmospheres only at temperatures of 2800° - 3700°K.[156] Many reactions have been reported for CO_2 at high temperatures, 350° - 1500°, that probably are independant of the prior decomposition of the CO_2. Hydrogen sulfide reacted with CO_2 between 350° and 900°

to give the following equilibrium[196]

$$H_2S + CO_2 \rightleftarrows 2H_2O + CS_2 \qquad (34)$$

which was postulated to be a two step process viz.

$$H_2S + CO_2 \rightleftarrows H_2O + COS \qquad (35)$$

$$H_2S + COS \rightleftarrows H_2O + CS_2 \qquad (36)$$

The reaction between CO_2 and CS_2 has been reported to occur on a glowing copper wire to form CO and S_2.[128] The CO formed reacted with the S_2 to give COS in a second step. This same paper reports the reaction of CO_2 and H_2S to yield CO, H_2O and S. In a high temperature study of CO_2 with B_2S_3 at 1500° in a Miker furnace the following reaction was reported[43]

$$3CO_2 + B_2S_3 \rightleftarrows B_2O_3 + 3CO + 3S \qquad (37)$$

No COS formation was reported here. Calcium cyanimide, $CaCN_2$,[68] was reported to react with CO_2 from 600° - 1000° by the equation

$$2CaCN_2 + CO_2 \rightarrow 2CaO + 3C + 2N_2 \qquad (38)$$

A second reaction occurs if excess CO_2 is present with the carbon viz.

$$CO_2 + C \rightarrow 2CO \qquad (39)$$

Carbon dioxide has been found to react readily with SF_4 at 500° to form COF_2.[93] Excess SF_4 gives CF_4 as the product. Sulfur is also formed in this reaction. These workers also report other related reactions at 500°.

$$3CO + SF_4 \rightarrow 2COF_2 + COS \qquad (40)$$

$$3CO + SOF_2 \rightarrow COF_2 + COS + CO_2 \qquad (41)$$

$$2CO + SF_4 \rightarrow 3CF_4 + 2SOF_2 + S \qquad (42)$$

Decomposition of carbonyl fluoride between 300° and 1200° went by the equilibrium[120]

$$2COF_2 \rightleftarrows CF_4 + CO_2 \qquad (43)$$

K_p for this process was reported at 1000°. Platinum or Nickel catalysts were employed in this decompostiion. Recently the reaction of CO_2 and CCl_4 was reported at 628° - 710°K and ΔH_r for the following reaction was calculated to be 16.8 Kcal/mole at 298°.[121]

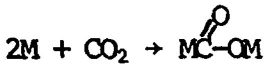
$$CO_2 + CCl_4 \rightleftarrows 2CO + 2Cl_2 \tag{44}$$

Besides the high temperature reactions of CO_2 that have been reported there are also some very interesting room temperature reactions. The fluorination of CO_2 with F_2 in the presence of CsF has been reported by two groups of workers to form $CF_2(OF)_2$ at 25°. The reaction proceeds quantitatively in either excess CO_2[37] or F_2.[190] Reaction time was 3 days and pressures of 3 atm were used by one group. The reduction of CO_2 occurs at room temperature in the presence of $LiAlH_4$ or $NaBH_4$.[205] Another reduction of CO_2[193] occurs in the reactions of CO_2 with P and CaO or CO_2 with Ca_3P_2 at moderate temperatures viz.

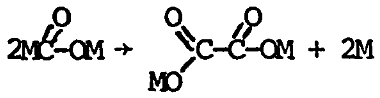
$$CO_2 + P + CaO \rightarrow Ca_3(PO_4)_2 + C \tag{45}$$

$$CO_2 + Ca_3P_2 \rightarrow Ca_3(PO_4)_2 + C \tag{46}$$

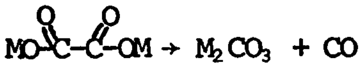
Carbon dioxide reacts with Cs or Rb[15] at room temperature to form Cs_2CO_3 and CO or analagously Rb_2CO_3 and CO. This reaction was proposed to proceed through the intermediate $M\text{-}\overset{O}{C}\text{-}OM$ by the following equations



$$2M + CO_2 \rightarrow M\overset{O}{\overset{\|}{C}}\text{-}OM \tag{47}$$



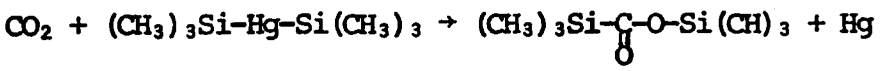
$$2M\overset{O}{\overset{\|}{C}}\text{-}OM \rightarrow MO\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OM + 2M \tag{48}$$



$$MO\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OM \rightarrow M_2CO_3 + CO \tag{49}$$

At 300° Cs and Rb react with CO_2 to give the oxide M_2O and CO.

Carbon dioxide has been reported to act as a weak Lewis acid and form a 1:1 adduct with tributylmethoxytin. Carbondioxide was found to replace Hg from $(CH_3)_3$-Si-Hg-Si$(CH_3)_3$ by the reaction[18]



$$CO_2 + (CH_3)_3Si\text{-}Hg\text{-}Si(CH_3)_3 \rightarrow (CH_3)_3Si\text{-}\underset{\overset{\|}{O}}{C}\text{-}O\text{-}Si(CH)_3 + Hg \qquad (50)$$

Another interesting insertion reaction with CO_2 occurs in the formation of the carbamate in the reaction of silyldimethylamine with CO_2 at 100° and 30 atm.[53] In a recent review the reactions of CO_2 with transition metal compounds are described.[200]

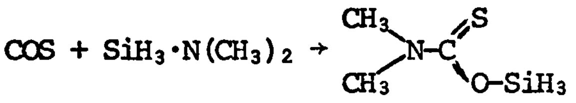
2. <u>Carbonyl Sulfide</u>: The chemistry of carbonyl sulfide has been reported in an extensive 1957 review by Ferm.[65] It has usually been prepared by the reaction of CO and S with varying reaction conditions. A novel reaciton of this type employs tributylamine and H_2S as the solvent system and the CO and S react at 90° and 6 atm pressure to give yields of 25%.[8] Carbonyl sulfide has been reported to decompose by two independant routes[164]

$$2COS \rightarrow CO_2 + CS_2 \qquad (51)$$

and

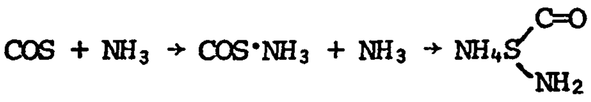
$$COS \rightarrow CO + S \qquad (52)$$

Carbonyl sulfide reacts similarly to CO_2 as it also is reduced by $LiAlH_4$ and $NaBH_4$.[205] It was found to react with dimethylsilylamine at 100° and 30 atm by the reaction[53]



$$COS + SiH_3\cdot N(CH_3)_2 \rightarrow (CH_3)_2N\text{-}C(=S)\text{-}O\text{-}SiH_3 \qquad (53)$$

in an analagous fashion to CO_2. Carbonyl sulfide forms a 1:1 adduct with ammonia[179] and in excess ammonia at 20° undergoes an interesting reaction viz.



$$COS + NH_3 \rightarrow COS\cdot NH_3 + NH_3 \rightarrow NH_4S\text{-}C(=O)\text{-}NH_2 \qquad (54)$$

At temperatures above 40° the $NH_4S(CO)NH_2$ decomposes to NH_3, COS and H_2S. Carbonyl sulfide has been fluorinated by an electrochemical process in liquid HF to give COF_2 and SF_6 as products.[146]

3. <u>Carbon Disulfide</u>: Carbon disulfide has a very interesting inorganic chemistry. It is quite thermally stable as evidenced by studies of its preparation and decomposition at high temperatures. Carbon disulfide has been reported to be formed in good yield from the decomposition of COS[125] at 440° - 500° by the reaction

$$2COS \rightarrow CO_2 + CS_2 \qquad (55)$$

Carbon disulfide has been reported by various workers to form in good yields by the direct union of C and S at temperatures of 750° - 1000°.[106,125] The type of carbon used was important. Wood charcoal or activated carbon reacted readily with sulfur at 750°; however, coke was very unreactive even at 1000°. Carbon disulfide is commercially prepared by the reaction

$$CH_4 + 4S \xrightarrow[500°-700°]{} CS_2 + 2H_2S^{106} \qquad (56)$$

As previously stated, CS_2, once formed is quite thermally stable. Carbon disulfide underwent decomposition in a shock wave apparatus with pressures up to 1000 atm at 1950° - 2800°K.[156] In two separate high temperature mass spectroscopy studies of CS_2 decomposition it was found that CS_2 began decomposing at 1300°K and the decomposition was complete at1900°K forming CS + S.[166] The CS_2 in this study was contained in a vitreous carbon cell. The carbon cell was found to react with CS_2 also viz.

$$CS_2 + C \rightarrow 2CS \qquad (57)$$

at 1900°K. In the second study[17] no decomposition of CS_2 was noted on pure carbon at 2100°K. Decomposition did occur on a carburized tungston rod at about 1700°K to give CS and S as products. The reaction of CS_2 with S has been studied by mass spectroscopy.[98] The reported equilibrium is

$$CS_2 + S \rightleftarrows CS + S_2 \qquad (58)$$

Polymers of CS_2 have been reported both of formula $(CS)n$[29,199] and $(CS_2)n$[108]. They are generally formed by CS_2 under extremely high pressures.

A variety of halogenation reactions of CS_2 have been reported. Iodine pentafluoride[94] and UF_6[198] reacted with CS_2 to give $(CF_3)_2S_2$ as the main product as reported elsewhere in this introduction. The UF_6 reaction is interesting since it also yields SF_4, UF_4 and $(CF_3)_2S_3$ at 25°. At higher temperatures SF_6 and CF_4 are also formed. Carbon disulfide has been fluorinated by the pentafluorides of V, Nb and Ta[40] and by the hexafluorides of Cr, Mo and W.[154] Halogenated derivatives of methane have been prepared from CS_2 by different methods. Carbon disulfide was found to react with HF and Cl_2[122] at 50° and 4.5 atm in 2 hour to give about 90% consumption of CS_2 by the reaction

$$CS_2 + 3HF + 3Cl_2 \rightarrow Cl_3CF + Cl_2CF_2 + CCl_4 \qquad (59)$$

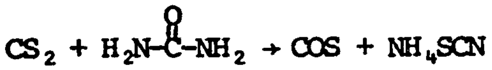
In a similar study done at higher temperatures with catalysis the halogenated methanes were specifically synthesized,[69] for example:

$$CS_2 + HF + Cl_2 \xrightarrow[CuCl]{200°-400°} CF_2Cl_2 \qquad (60)$$

and

$$CS_2 + HF + Cl_2 \xrightarrow[CrF_3]{450°-500°} CFCl_3 \qquad (61)$$

Carbon disulfide has been reduced by $LiAlH_4$ or $NaBH_4$ in a manner similiar to CO_2 and COS.[205] It reacts with liquid SO_3 at room temperature forming SO_2, COS, S and a viscous brown polymer which contains both C-O and C-S groups in sulfur chains.[192] These workers report no reaction between CS_2 and SO_3 in the gas phase at temperatures up to 400°. Carbon disulfide has been reported to react with the complex salt $[AsCl_4][AsF_6]$ which had been prepared at 0° by the reaction of AsF_3 and Cl_2.[122] Urea dissolved in low molecular weight alcohols (C_1-C_4) reacts with CS_2 in a closed vessel under autogenous pressure at 120°-160° to give the following reaction in a 90% yield[147].



$$CS_2 + H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \rightarrow COS + NH_4SCN \qquad (62)$$

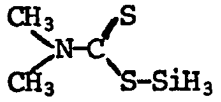
Carbon disulfide reacts with liquid ammonia[167] and with concentrated aqueous solutions of alkali bases[187] to form thiocarbonates containing the CS_3^{-2} ion.

$$CS_2 + NH_3 \rightarrow (NH_4)_2CS_3 + NH_4SCN \qquad (63)$$

$$CS_2 + MOH \rightarrow M_2CS_3 + \text{other products} \qquad (M = Cs, Rb, K) \qquad (64)$$

These thiocarbonates give sulfates upon direct oxidation at about 250°. At higher temperatures H_2O hydrolizes the M_2CS_3 compounds to $M_2S + H_2S + CO_2$.

Carbon disulfide forms adducts with some substances like $(C_4H_9)_3SnOCH_3$[18] and $HRe(CO)_3$ (diphenylphosphinoethane). Carbon disulfide reacts with $(CH_3)_3E\text{-}As(CH_3)_2$[1] where E = Si, Ge or Sn. Like CO_2, CS_2 reacts with dimethyl silyamine[53] and bistrimethyl silylmercury[148] to give



and $(CH_3)_3Si\text{-}C\text{-}S\text{-}Si(CH_3)_3$

respectively.

I. Chemistries of Sulfur Dioxide and Hydrogen Sulfide

This section will include only a brief survey of SO_2 and H_2S reactions as the literature on the compounds is extensive. Reactions relevent to this dissertation have been included along with some other unique reactions of SO_2 and H_2S.

1. Sulfur Dioxide: Johnstone in 1942 reviewed the chemistry of SO_2.[103] A number of recent reports discuss a variety of halogenation reactions of SO_2. Sulfur dioxide was reported to react with CCl_4 or $CHCl_3$ in the presence of $AlCl_3$ at pressures up to 950 atm to form $SOCl_2$ in 70-80% yields.[67] The reaction of SO_2 with PCl_3[188] has been studied from 298°K to 1500°. The reaction which occurs at higher temperatures is

$$SO_2 + PCl_3 \rightarrow OPCl_3 + SO \qquad (65)$$

The SO formed was unstable and disproportionates viz.

$$2SO \rightarrow SO_2 + S \tag{66}$$

$SPCl_3$ was also found in trace amounts due to the reaction

$$S + PCl_3 \rightarrow SPCl_3 \tag{67}$$

Sulfur dioxide reacted with ClF to give $ClSO_2F$ in excellent yields.[176] Various workers have reported the reaction of SO_2 with difluorodiazine, N_2F_2. Lustig reports that mixtures of sulfur fluorides and oxyfluorides are formed.[124] Roesky,[173] et.al. report that SO_2 and N_2F_2 react at 300° to form SO_2F_2, SOF_2 and N_2O. The same paper reports that N_2F_2 reacts with SF_4 to form $SF_6 + N_2 + SO_2$ at 300°. The N_2F_2 is generated by the reaction

$$2NaN_3 + 4F_2 \rightarrow 3N_2F_2 + 2NaF \tag{68}$$

Sulfur dioxide has been halogenated photochemically in a glass reactor by a number of halosulfur compounds.[61] The reactions are interesting and show that the products come from reaction with the glass reactor as well as the reactants. The reactants were all irradiated with a Hg lamp ($\lambda = 2537\text{Å}$) for 48 hours.

$$SO_2 + F_3SCl \rightarrow SOF_2 + SO_2F_2 + SO_2Cl_2 + SiF_4 \tag{69}$$

$$SO_2 + (F_5S)_2O_2 \rightarrow F_3SCl + SOF_2 + SO_2F_2 + SO_2Cl_2 + SiF_4 \tag{70}$$

$$SO_2 + S_2F_{10} \rightarrow F_3SCl + SOF_2 + SO_2F_2 + SO_2Cl_2 + SiF_4 \tag{71}$$

Liquid SO_2 reacted with $F_5S\text{-}OF$ to form the addition product $SF_5\text{-}O\text{-}SO_2F$.[165] In other reactions where SO_2 has exhibited Lewis base properties, It was found to form an adduct with AsF_5 with the formula $AsF_3 \cdot SO_2 \cdot F_2$.[31] Other SO_2 adducts are known like $AsF_5 \cdot SO_2 \cdot SO_2F_2$ also. Sulfur dioxide exhibits Lewis acid properties also and addition compounds have been reported where SO_2 is the acceptor. Sulfur dioxide reacts with $(CH_3)_3N$ to form the 1:1 adduct $(CH_3)_3N \cdot SO_2$.[32] Sulfur dioxide also forms a 1:2

adduct with $(CH_3)_3NO$ at -80° which decomposes to the stable 1:1 adduct at room temperature via the equation

$$(CH_3)_3NO + 2SO_2 \xrightarrow{-80°} (CH_3)_3NO(SO_2)_2 \xrightarrow{RT} (CH_3)_3NOSO_2 + SO_2 \qquad (72)$$

No reaction has been observed between SO_2 and $(CH_3)_3NSO_3$. Sulfur dioxide acceptor properties are observed in complexes with halide ions in acetonitrile solution[153] like

$$(C_2H_5)_4N^+X^- + SO_2 \rightarrow (C_2H_5)_4N^+SO_2X^- \qquad (73)$$

where X = Cl, Br, I

Sulfur dioxide has also been reported to form 1:1 adducts with ethylene oxide, anisole and $(C_2H_5)_2S$ and with dioxane both 1:1 and 1:2 adducts are known.[3] The reaction of SO_2 with $(CH_3)_3P$ to give $(CH_3)_3PO$ and S has been reported.[190] Triphenyl phosphine reacted much more slowly with SO_2 but yielded $(C_6H_5)_3PO$ and $(C_6H_5)_3PS$ as products.[190] Another report of this type reaction where SO_2 reacted with XYZP in liquid phase at 50° for for long periods of time gave both XYZPO and XYZPS. It was noted that in excess SO_2 the XYZPS reacted to form XYZPO and S. (X,Y,Z = alkyl, aryl, alkoxy, Cl, Br, NCO or NCS).[66] The reaction of SO_2 with the complex salt $[Cl_3P:NPCl_2]^+[PCl_6]^-$ gave $OPCl_3 + Cl_3P:NPCl_2$ + other products.[14] Sulfur dioxide reacts similiarly to CO_2 and CS_2 in replacing Hg in the reaction[148]

$$SO_2 + (CH_3)_3SiHg\cdot Si(CH_3)_3 \rightarrow (CH_3)_3Si\text{-}O\text{-}S\text{-}OSi(CH_3)_3 + Hg \qquad (74)$$

Sulfur dioxide was reduced by $NaBH_4$ or $LiAlH_4$ in a variety of organic solvents to give H_2S quantitatively on hydrolysis.[182] Sulfur dioxide and Br_2 were used to oxidize Re, W and Mo in sealed tubes at 400° to give products such as ReOBr, WO_2Br_2 and $MoBr_3$.[55] Sulfur dioxide has been used as a reducing agent for UF_6 being photochemically reduced to UF_5.[92] In a high temperature study SO_2 was found to react with GeS[113] viz

$$SO_2 + GeS \rightarrow S + GeO_2 + Ge_2S \qquad (75)$$

The reaction began at 400° but a good yield was not obtained until temperatures > 600°. The Ge_2S formed reacted with excess SO_2 at 700°-800° to give $GeO_2 + S$. The reaction of SO_2 with a mixture of CS_2 and COS was reported to be complete but very slow at low temperatures forming $CO_2 + S$.[10]

2. Hydrogen Sulfide: Hydrogen sulfide has been prepared from the reaction of phosphine and sulfur at 450°[48] viz.

$$PH_3 + S \rightarrow H_2S + P_xS_y \text{ mixture} \qquad (76)$$

The reaction between PH_3 and H_2S has been reported to occur above 320° to be

$$PH_3 + H_2S \rightarrow H_2 + P_xS_y \text{ mixture.} \qquad (77)$$

No reaction occured below 320°. In other reactions with phosphorus compounds H_2S was reported not to react with $(C_6H_5O)_3P$ unless $(C_2H_5)_3N$ was present, in which case, the adduct $(C_6H_5O)_3P\cdot(C_2H_5)_3N\cdot 2H_2S$ was formed.[2] The adduct $(C_2H_5)_3N\cdot H_2S$ which is prepared at -5° was found to react with $(C_6H_5O)_3P$ to give $(C_6H_5O)_2P\cdot HS$ with a 30% yield. The adducts $(C_2H_5)_3NH^+HS^-\cdot 2H_2S$ and $(CH_3)_4NHS\cdot 3H_2S$[130] have also been reported.

Various halogenation reactions of H_2S are reported UF_6.[198] reacts with H_2S at 25° by the reaction

$$H_2S + UF_6 \rightarrow UF_4 + SF_4 + HF \qquad (78)$$

Diphosphorus tetraiodide[13] in benzene reacts with H_2S to yield $P_4S_3I_2$. Highly reactive O_2F_2[191] oxidizes and fluorinates H_2S at low temperatures to give mixtures of sulfur oxides and fluorides. Silicondifluoride has been reported to form a low temperature polymer with H_2S which decomposes on warming to room temperature to give SiF_2HSH, SiF_2HSiF_2SH and Si_2F_5H.[183] The room temperature reaction of H_2S with SO_2Cl_2 in different solvents has been reported.[177] In anhydrous benzene with excess SO_2Cl_2 the reaction proceeds viz.

$$H_2S + SO_2Cl_2 \rightarrow HCl + SO_2 + S \qquad (79)$$

In excess H_2S the reaction products differ:

$$H_2S + SO_2Cl_2 \rightarrow HCl + H_2O + S + S_2O \qquad (80)$$

The workers also investigated this reaction in ethyl ether. For excess SO_2Cl_2:

$$H_2S + SO_2Cl_2 \rightarrow HCl + SO_2 + H_2SO_4 + H_2O + SCl_2 + S_2Cl_2 \qquad (81)$$

and in excess H_2S:

$$H_2S + SO_2Cl_2 \rightarrow HCl + H_2O + S + \text{sulfanes} \qquad (82)$$

were found in the reaction mixture. The low temperature reactions of H_2S with FSSF, SSF_2, SF_4 and SOF_2 were recently reported.[127] The liquid phase reaction of H_2S and $VOCl_3$ has been reported[30] to yield $VSCl_3$ and VOHSHCl. These workers also report that no reaction occured between liquid SO_2 and $VOCl_3$. Boron tetrachloride[204] forms low temperature adducts with H_2S at -78.5° but at 90° the following reaction takes place

$$4H_2S + 3B_2Cl_4 \rightarrow 2BCl_3 + 2B_2S_2 + 4H_2 \qquad (83)$$

Hydrogen sulfide reacts with borontrihalides (Cl, Br, I) and forms a variety of substitution products depending on the H_2S concentration.[24]

$$H_2S + BX_3 \rightarrow BX_2SH + BX(SH)_2 + B(SH)_3 + HX \qquad (84)$$

Hydrogen sulfide was used to form the transition metal chalcogen compound $CuNH_4WS_4$[141] in a 32% yield by the reaction

$$CuSO_4 \cdot 5H_2O + WO_3 + H_2S \xrightarrow[NH_4OH]{} CuNH_4WS_4 \qquad (85)$$

Hydrogen sulfide has been reported in a synthesis of concentrated aqueous hydroiodic acid[96] viz.

$$H_2S + I_{2\,(aq)} \rightarrow 2HI_{(aq)} + S \qquad (86)$$

The reaction of H_2S with HgI_2 has also been reported[139] where HI is formed by the equations:

$$2HgI_2 + H_2S \xrightarrow[H_2O]{} 2HgI + 2HI + S \tag{87}$$

$$2HgI + H_2S \rightarrow 2HgS + 2HI \tag{88}$$

CHAPTER II

EXPERIMENTAL

A. Vacuum System Equipment and Techniques.

The basic principles of vacuum line techniques have been described elesewhere.[104] Therefore, only the aspects pertaining to this work are summarized here.

1. Vacuum System: The vacuum system was constructed of borosilicate (Pyrex 7740) glass and equipped with precision ground glass or teflon (Fischer and Porter #705-005-0004) stopcocks. All ground glass stopcocks and joints were lubricated with Apiezon M grease. The system was evacuated using a Model 1400 Welch Duo Seal fore-pump in series with a liquid nitrogen traps. A VacTorr 25 (Precision Scientific Co.) pump was also used for the latter part of this research. The vacuum system was evacuated to 10^{-3} - 10^{-4} torr (1 torr = 1 mm Hg) before handling a material. A section of the vacuum system was calibrated so that its volume was known. This facilitated quantitative determination of gaseous materials. (See Figure 1)

2. Pressure Measurements: Pressure measurements, below atmospheric pressure, were made using a mercury manometer. The pressure was read with a meter stick calibrated in millimeters and could be read to approximately ± 0.3 mm.

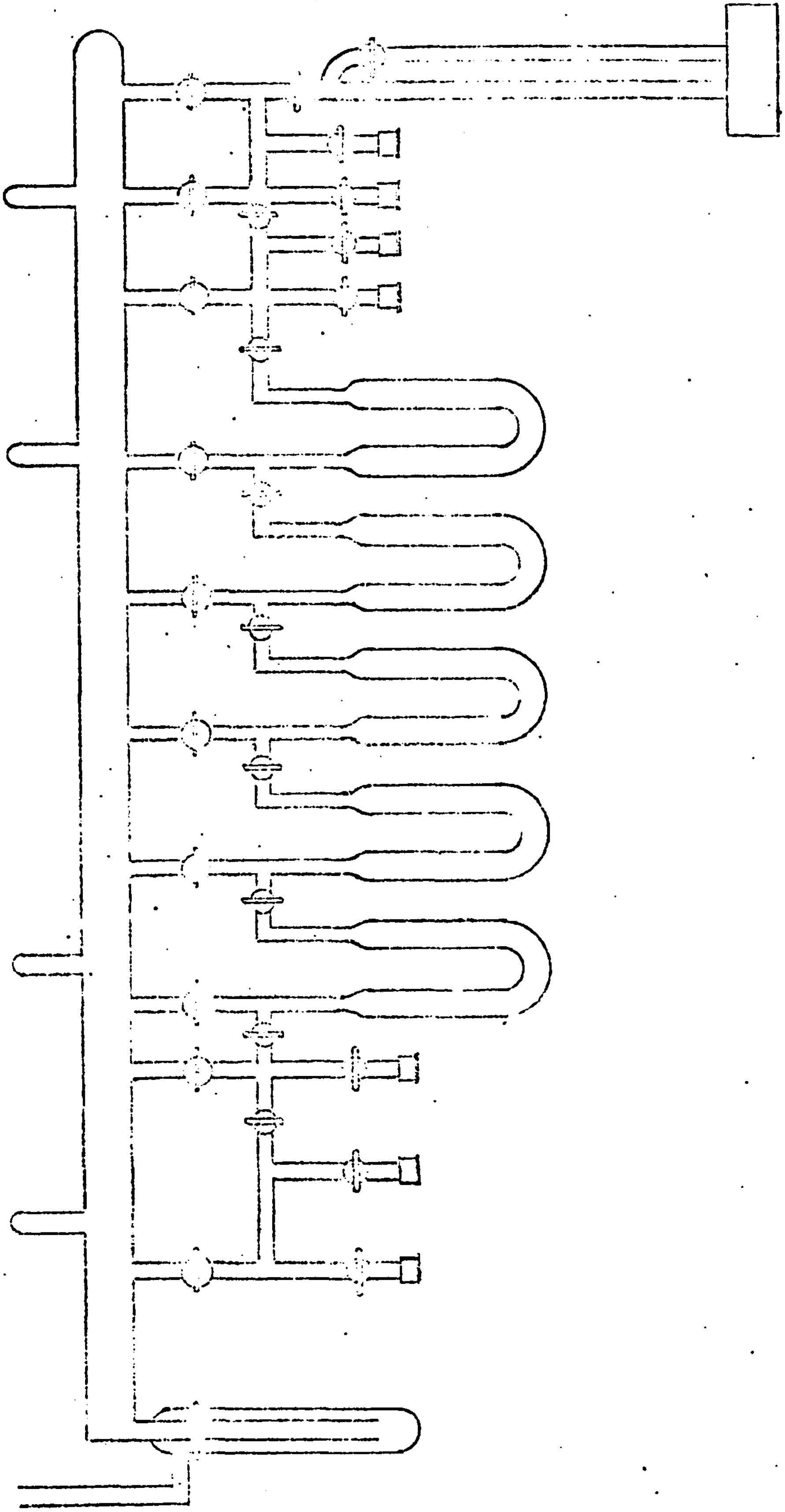


Figure 1 Vacuum System

3. Temperature Measurements: Low temperature measurements were made using a pentane in glass thermometer (range +30° to -200°, accurate to ±2°). Room temperature measurements for molecular weight determinations or for other quantitative molar volume determinations were made with a thermometer which could be read to ± 0.3° suspended from the vacuum system.

4. Production of Low Temperatures: Liquid nitrogen in Dewar flasks was used to maintain temperatures at -196°. A mixture of dry ice and either acetone or isopropanol in a Dewar falsk was used for maintaining temperatures around -78°. A variety of below ambient temperatures were achieved by making "slush" baths of a variety of organic solvents. The appropriate solvent was frozen in liquid nitrogen in a Dewar flask and then warmed to the melting point of the solvent. The bath would then maintain the temperature of the melting point (solid - liquid equilibrium) of the solvent for a period of time. See Table III for a list of slush baths used in this research.

5. Production of High Temperatures: When temperatures above ambient were needed for rapid warming of a frozen sample, a heat gun (Heat Blo 5000, Milwaukee Lock and Mfg. Co.) was employed.

6. Separation of Volatile Materials: Mixtures of volatile materials were separated by fractional condensation in, or distillations from, traps maintained at low temperatures. The notations used to describe the various separations are as follows:

$$\begin{array}{llllll} RT \sim & -96^\circ & \sim -196^\circ & \text{(n times)} & & \\ & (A) & \quad\downarrow & & & \\ & & RT \sim & -134^\circ & \sim -196^\circ & \text{(n times)} \\ & & & (B) & \quad (C) & \end{array}$$

This means that a mixture was allowed to warm to room temperature and then passed through a -96° trap to another trap at -196° without pumping.

TABLE III

Liquids and Mixtures Suitable for Constant Low Temperature Baths Used in the Research[a]

Compound	Approximate Freezing Point °C
Carbon Dioxide[b]	- 78
Toluene	- 96
Methylcyclohexane	-126
n Pentane	-130
n Pentane, isoPentane	-145
isoPentane	-160
Nitrogen	-196

[a] A "slush" bath in which solid - liquid equilibrium is maintained

[b] The -78° bath is dry ice with acetone or iospropanol as the conductive solvent.

The symbol " ∿ " signified that the material is passing from a trap at one temperature to a trap at another temperature. The (n times) represents the number of times a trapped material is redistilled. For example if n = 3 then the following operations were carried out on a particular fraction:

$$\begin{array}{lll} RT \sim -96^\circ \sim -196^\circ & & (n = 1) \\ \downarrow & & \\ \quad RT \sim -96^\circ \sim -196^\circ & & (n = 2) \\ \quad\quad \downarrow & & \\ \quad\quad RT \sim \underset{(A)}{-96^\circ} \sim -196^\circ & & (n = 3) \end{array}$$

The fraction (A) could then be examined to access whether only that material which should stop in the -96° trap was present. The process ends when n is reached, that is, when no more material is present in the -196° trap. The verticle arrow " ↓ " indicated that a new distillation scheme was employed. The process continues with the separation of the material which passed the first trap. The capital letter under each temperature implies that this was a separate fraction which was later identified. If no letter appears under a particular temperature, then this implies that either nothing was present in the trap or that no attempt was made to identify the material.

This technique was used to separate the reactants and products from a reaction mixture as well as a purification method for reactant materials.

7. Molecular Weight Measurement: The molecular weight of volatile compounds was carried out using a vapor density method. In such determinations the gas was assumed to follow the ideal gas equation as the pressure did not exceed 0.5 atmospheres. Therefore, the weight of the gas at a known temperature, pressure and volume permitted the calculation of the molecular weight from the equation of state for a perfect gas:

$$PV = nRT = \frac{g}{MW} RT \qquad (89)$$

Therefore $$MW = gRT/PV \qquad (90)$$

Where MW = Molecular weight

g = Weight of the sample in grams

R = Gas constant 0.0821 $\frac{\ell \text{ atm}}{\text{mole } ^\circ\text{K}}$

T = Temperature, °K

P = Pressure in atmospheres

V = Volume in liters

Care was taken not to carry out molecular weight determinations at the saturation vapor pressure at room temperature of the materials under study. In such circumstances the molecular wieght could be erroneous due to adsorption on the glass surface of the molecular weight bulb.

8. Melting Point Measurements: The melting points of solid materials was determined with the use of a standard melting point apparatus (GallenKamp, MF - 370). The accuracy with which melting points could be determined was approximately ± 1°.

9. Criteria of Purity: The purity of materials used in this research was checked by at least two of the following procedures:

a. Molecular weight so that the error in the difference between the calculated and experimental values did not excees 1% of the calculated value.

b. Infrared spectrum to agree with a published spectrum or to a spectrum previously determined in this laboratory on the pure material.

c. Mass spectrum to agree with a published spectrum or to a spectrum previously determined in this laboratory on the pure material.

d. Melting point determinations to ± 1° of the literature value and a range not exceeding 1.5°.

10. Determination of Reaction Yields: The yield or percent conversion of a reaction was determined by one of the following ways.

a. If the reactant mixture could be totally separated, the yield was calculated on the percent consumption of one or more of the reactants.

b. The yield was sometimes calculated on the amount of one of the products formed if it was completely isolated from the reaction mixture.

c. Some yields were based on an amount of noncondensible gas formed if the rest of the reaction mixture could not be adaquately separated.

d. In some cases yields were determined on reactions that could not be separated, but where all reactants and products were known, where a balanced equation could be written, and where there was either a net gain or loss between total moles or reactants and total moles of the reaction mixture.

In all cases, yields were assumed to accurate to ± 3% as this was the acceptable limit of recovery of a sample of nonreacting gas.

e. The composition of binary mixtures of gases was calculated from the set of equations when both the total moles and total weight of the mixture was known.

$$(1)\quad nt = n_A + n_B \tag{91}$$

$$\text{so}\quad nt = \frac{g_A}{MW_A} = \frac{g_B}{MW_B} \quad \text{and} \tag{92}$$

$$(2)\quad gt = g_A + g_B \quad \text{where} \tag{93}$$

nt = total moles of mixture

n_A, n_B = moles of component A and B

MW_A, MW_B = molecular weights of components A and B gt = total weight of mixture

g_A, g_B = weights of components A and B

B. High Pressure Equipment and Techniques

1. General Description of High Pressure Apparatus: The high pressure system was designed by Dr. J. J. Moscony and Professor A. G. MasDiarmid to be used in conjunction with a high vacuum system. The intensifier and microreactors were purchased from HIP-Autoclave Engineers, Erie, Pennsylvania. The details on the model system have been published by Moscony, Harker and MacDiarmid.[140] A Diagram of the model system is shown is Appendix I. The system has been modified in this laboratory by the addition of an electric motor to power the hydraulic pump. Also added is a heater system (Tem Press Research Model HR 1 B 4) equipped with four heaters each with its own pressure gauge and temperature settings making it possible to run four high pressure reactions simultaneously while monitoring the temperature and pressure of each. The microreactors were rated at 600° and 4000 atm. The temperature was measured by use of a thermocouple placed in a well in the bottom of the microreactor. A Leeds and Northrup potentiometer (model 8690) was used with the thermocouple. (See Figure 2)

The high pressures obtained in this research warrant caution at all times. The intensifier used in this research was enclosed in one quarter inch steel plate. Care was exercised never to exceed the limits of the microreactors or the rest of the system. Safety goggles, leather gloves and a leather jacket were available for use.

2. High Pressure Techniques and Gold Tube Handling: The technique employed in this research was developed by Hagen[80] and involves the use of malleable, nonreactive material to encapsulate the reactants and the use of nitrogen gas as the external pressuring medium. The capsule or ampule containing

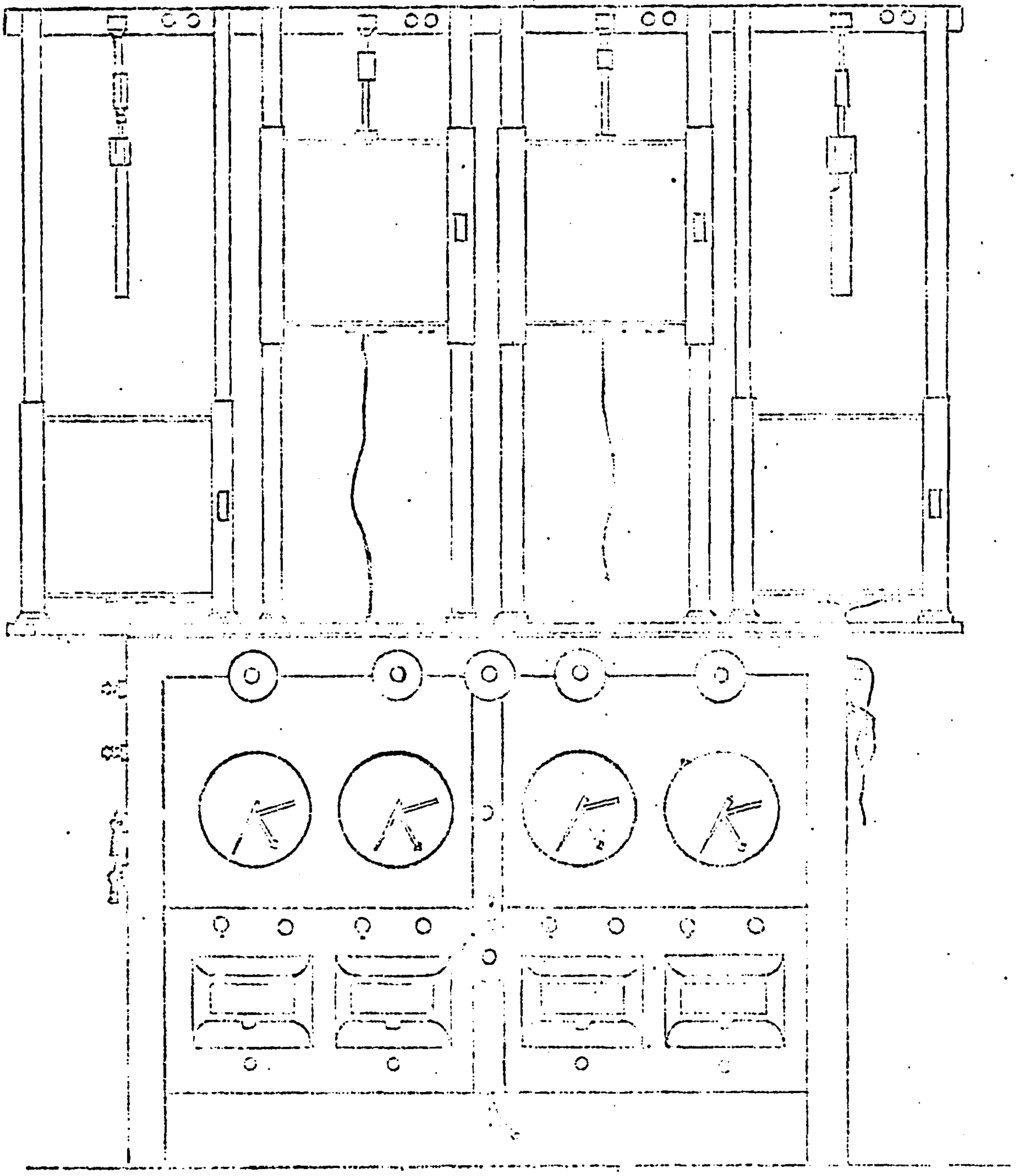


Figure 2 Hydrothermal Apparatus

the reacting materials is placed in a microreactor and pressured and heated to the desired pressure and temperature.

The technique is best illustrated by the following step by step Description:

(1) A length of gold tubing (2.0 mm o.d., 2.9 mm i.d., 8 cm or more in length) was flattened for 1 cm at one end with a pair of pliers whose jaws are cushioned with tape. The flattened end of the gold tube was then heated in a H_2/O_2 glass blowers torch, melting the gold and sealing the end of the tube.

(2) The open end of the gold tube is fitted into the tapered end of a ₷ 12/30 male joint. The glass-gold junction is heated in an open flame and "black wax" (picein wax was applied to the hot junction which upon cooling forms a vacuum tight seal. (See Figure 3)

(3) The gold tube was then evacuated and flamed with a H_2/O_2 with pumping. The tube was allowed to stand open to a manometer for one hour. If no pressure was observed the tube was declared leak free.

(4) A moistened piece of asbestos tape was placed around the "black wax" seal to prevent the wax from melting when the tube was finally sealed (step 9).

(5) At this point the tube was removed from the vacuum system if a solid reactant was to be added. If a solid was put in the tube, it was weighed in difference from a weighing bottle. The gold tube containing the solid was then put back on the vacuum line and carefully evacuated.

(6) If one of the reactants was a liquid, the tube might also have been removed from the vacuum line, the liquid added by use of a syringe, the tube would then be alternately warmed to room temperature, frozen to -196° and degassed two or three times before continuing.

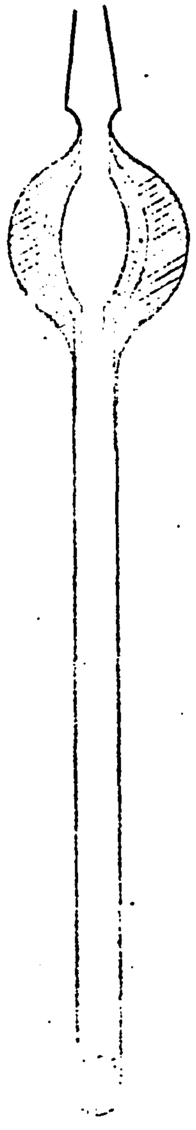


Figure 3 Gold Tube Prepared for Sealing

(7) In most cases in this research both reactants were gases. From (step 4) the first reactant gas was condensed into the gold tube at -196° The amount of material condensed in was previously determined using the ideal gas equation where the volume was a calibrated volume on the vacuum line, the pressure was read on the manometer and the temperature was the room temperature measured with a thermometer suspended from the vacuum line. A Dewar flask of liquid nitrogen was continuously kept around the gold tube from this point.

(8) At this time, the second component was condensed into the gold tube in a similar manner as in step (7).

(9) The gold tube was then flattened with the padded pliers at a point just above the top of the Dewar flask. The flattened portion was about 2 cm in length. The gold tube was then sealed with a H_2/O_2 flame; hot, pointed and about 6 cm long. The seal was made as close to the liquid nitrogen as possible and the gold tube was held with a pair of forceps just below the seal. The sealed ampule was then tagged with a tabbed copper wire until pressurization. The ampule was stored in this fashion in liquid nitrogen.

(10) When the gold tube was ready to be reacted, the wire was removed and the tube was quickly transferred to a microreactor which was cooled to -196°.

(11) The microreactor was then fitted to the intensifier still at -196° and pressured. The Dewar of liquid nitrogen was removed and the microreactor was pressured and heated to the reaction conditions for a period of time of from 18 to 24 hours, usually.

(12) After reaction time the furnace was removed and the microreactor cooled to room temperature and was then cooled to -196°. The pressure

was released and the microreactor was clamped in a vise, opened, and the gold tube was quickly transferred to a Dewar flask of liquid nitrogen. The tube was usually flat except where any solid material was positioned.

(13) The gold tube opener was connected to the vacuum line through the side arm. Glass beads were positioned in the lower portion of the opener to adjust the level of the gold tube.

(14) The glass cap was removed from the top of the opener and the gold tube was quickly dropped in to the opener and the cap replaced. The opener was immediately evacuated and the gold tube was checked for leaks. After pumping away water vapor and CO that had frozen to the outside of the gold tube, the cutter was left open to the manometer to again check for leaks. (See Figure 4)

(15) The gold tube was opened by turning the straightbore stopcock through the gold tube, cutting it in two. As the tube was cut the volatiles in the tube were trapped in the vacuum line at -196°. Any noncondensible gases were observed, and after pumping out the cutter, the cutter was removed from the line and the gold tube was recovered and cut open to see if any solids were present.

(16) At this point the volatile material was identified using standard vacuum techniques.

C. Spectroscopic Equipment and Techniques

1. Infrared Absorption Spectra: Infrared absorption spectra were obtained using either a Beckman IR-8 or Beckman IR-10 double beam, grating spectrophotometer. The instrument was calibrated after each spectrum with a polystyrene film.

Spectra of volatile materials were obtained in a 100 mm gas cell fitted with KBr windows sealed with rubber O-rings at reduced pressure. Spectra of solid materials were obtained either in a Nujol mull or in a

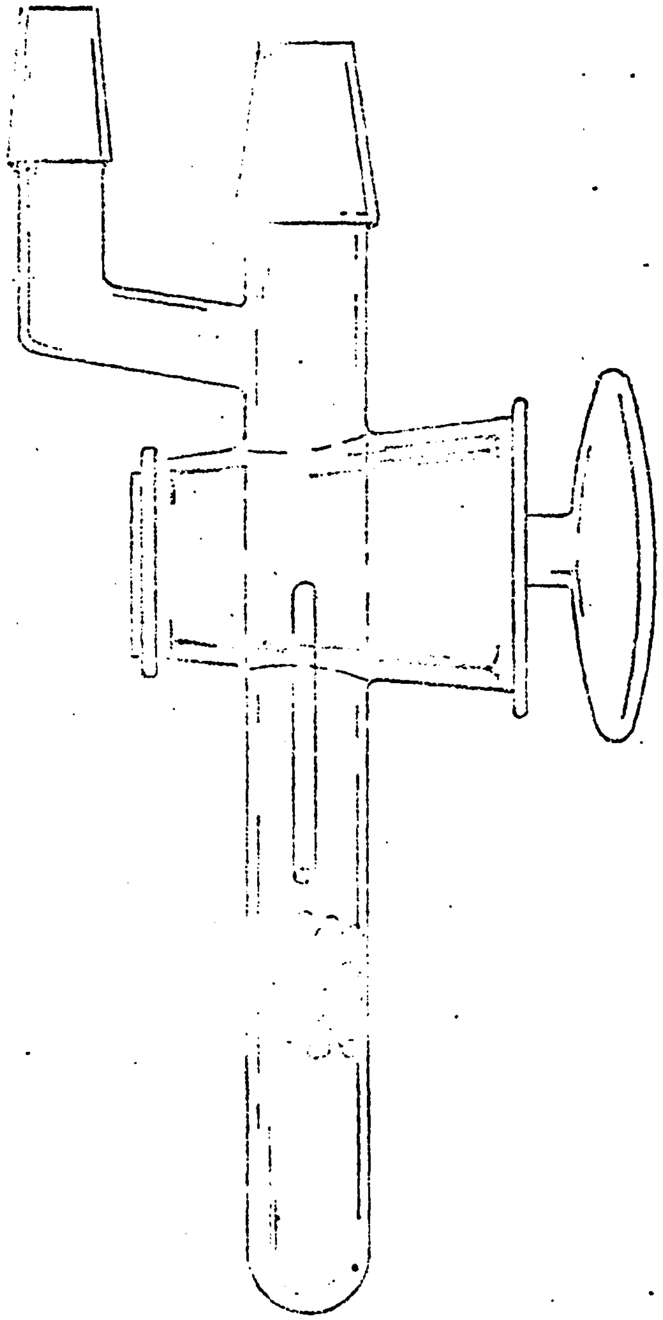


Figure 4 Sealed Tube Opener

KBr pellet.

2. Mass Spectra: Mass spectral cracking patterns were obtained using a Hitachi - Perken Elmer RMU - 7E Mass Spectrometer. The instrument was operated at an ionizing potential of 70 eV, current of 50 μA, ion source temperature of 150°, accelerating potential of 3,600 V and a pressure of between 10^{-6} and 5×10^{-5} torr.

All samples run were admitted through the gas inlet at room temperature.

D. Reagents.

Bisperfluoromethyl Disulfide - ($(CF_3)_2S_2$, Columbia Organic Chemicals Co.) was purified by distillation:

RT ∿ -78° ∿ -96° ∿ -196° (3 times)
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; the infrared spectrum was identical to the published spectrum.[28]

Carbon - (C, Sterling MT 2700° Graphitized Carbon, Cabot Corporation) was used as obtained after drying at 135° for 24 hours.

Carbon Dioxide - (CO_2, Matheson) was purified by distillation:

RT ∿ -96° ∿ -145° ∿ -196°
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; infrared[169] and mass spectra identical to that given in the literature.

Carbon Disulfide - (CS_2, Allied Chemical, reagent ACS) was purified by distillation:

RT ∿ -78° ∿ -96° ∿ -196° (3 times)
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; infrared[206] and mass spectra identical to that given in the literature.

Carbon Monoxide - (CO, Union Carbide, CP grade) was used after pumping through two traps cooled to -196°.

Carbon Tetrafluoride - (CF_4, Freon 14, Matheson) was purified by distillation:

RT ∿ -130° ∿ -161° ∿ -196° (3 times)
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; the infrared[72] and mass spectra[7] were identical to that given in the literature.

Carbonyl Sulfide - (COS, Matheson) was purified by distillation:

RT ∿ -96° ∿ -145° ∿ -196° (3 times)
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded: the infrared[33] and mass spectra were identical to that given in the literature.

Chlorotrimethyl Silane - ($(CH_3)_3SiCl$, Aldrich, tech.) was used to pretreat vacuum line and was used as obtained.

Gold Tubing - Mathey Bishop, Inc., Malvern, Pa. was used as obtained after flaming with methane oxygen torch.

Hydrogen Sulfide - (H_2S, Matheson) was purified by distillation:

RT ∿ -96° ∿ -145° ∿ -196° (3 times)
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; the infrared[4] and mass spectra were identical to that given in the literature.

Nitrogen - (N_2, Big 3 Industries) was used as obtained as an intensifying medium for the high temperature apparatus.

Phosphorus Pentafluoride - (PF_5, Matheson) was purified by distillation:

RT ∿ -96° ∿ -130° ∿ -196° (3 times)
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; infrared spectrum was identical to the published spectrum[79]; confirmed by mass spectrum.[174]

Phosphorus Trifluoride - (PF_3, Ozark, Mahoning Co., Lot. No. KS7-105) was purified by distillation:

RT ∿ -96° ∿ -145° ∿ -196°
(A) (B) (C)

Fraction (B) was retained and fractions (A) and (C) were discarded; infrared[79] and mass spectra[174] identical to that given in the literature; mol. wt. calc'd 87.97, found 88.1)

Sulfur - (S, Mallinckrodt) dried at 60° for 24 hours and used as obtained.

Sulfonyl Fluoride - (SOF_2) was obtained by purifying a reaction mixture of SF_4 + SiO_2. Sulfur tetrafluoride was condensed into the vacuum line and allowed to react with the glass walls for 2 hours. The resulting mixture was separated as follows:

RT ∿ -130° ∿ -196° (6 times)
(A) (B)

Fraction (A) was retained while fraction (B) which contained SiF_4 and some SOF_2 was discarded. The infrared spectrum of (A) was identical with the published spectrum of SOF_2.[155]

The SOF_2 was also separated from the reaction mixture of CS_2 and $(CF_3)_2S_2$ at 540° and 4000 psi. The mixture was separated as follows:

RT ∿ -96° ∿ -130° ∿ -196° (3 times)
(A) (B) (C)

Fraction (A) contained CS_2 and was discarded. Fraction (B) was retained and contained SOF_2. Fraction (C) contained SiF_4, CF_4 and some SOF_2 and was discarded. The infrared spectrum of (B) was identical with the published spectrum of SOF_2.[155]

Sulfur Dioxide - (SO_2 Matheson) was purified by distillation:

$$\text{RT} \sim \underset{(A)}{-95°} \sim \underset{(B)}{-126°} \sim \underset{(C)}{-196°} \qquad \text{(3 times)}$$

Fractions (B) was retained and fractions (A) and (C) were discarded; infrared[184] and mass spectra identical to that given in the literature.

Sulfur Hexafluoride - (SF_6, Matheson) was purified by distillation:

$$\text{RT} \sim \underset{(A)}{-95°} \sim \underset{(B)}{-145°} \sim \underset{(C)}{-196°} \qquad \text{(3 times)}$$

Fraction (B) was retained and fractions (A) and (C) were discarded; infrared[116] and mass spectra were identical to that given in the literature; mol. wt. calc'd 146.06, found 146.1.

Sulfur Tetrafluoride - (SF_4, Matheson) was used to pretreat the vacuum line and was used as obtained.

E. High Pressure Reactions

1. The PF_3 - SF_6 System

a. The Reaction of Phosphorus Trifluoride and Sulfur Hexafluoride at 485°/4000 atm

Summary: It was found that PF_3 and SF_6 reacted at 485°/4000 atm according to the equation

$$3PF_3 + SF_6 \rightarrow 3PF_5 + S \qquad (94)$$

Phosphorus trifluoride (77 mg, 0.87 mmol) and sulfur hexafluoride (131 mg, 0.90 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 485°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material could not be separated by trap to trap distillation.

The following materials were identified.

PF_5 (110 mg, 0.87 mmol) and SF_6 (89 mg, 0.61 mmol); 100% reaction based on PF_3 consumed; infrared[79, 116] and mass[174] spectra identical with that expected for a mixture of PF_5 and SF_6.

Sulfur (9.3 mg, 0.29 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

An additional experiment in which similiar quantities of reactants were used resulting in reaction with the same products is summarized in Tables IV and XII.

b. The Attempted Reaction of Phosphorus Trifluoride and Sulfur Hexafluoride at 400°/4000 atm.

Summary: It was found that PF_3 and SF_6 did not react at 400°/4000 atm.

Phosphorus trifluoride (77 mg, 0.88 mmol) and sulfur hexafluoride (131 mg, 0.90 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 400°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\text{RT} \sim \underset{(A)}{-160^\circ} \sim \underset{(B)}{-196^\circ} \qquad \text{(2 times)}$$

The following materials were identified

A SF_6 (130 mg, 0.90 mmol; 100% recovery; identified by infrared spectrum[116]).

B PF_3 (77 mg, 0.88 mmol; 100% recovery; identified by infrared spectrum[79]).

Additional identical experiments in which similiar quantities of reactants were used resulting in no reaction are summarized in

Tables IV and XII.

c. The Reaction of Phosphorus Trifluoride and Sulfur Hexafluoride at 450°/4000 atm.

Summary: It was found that PF_3 and SF_6 reacted at 450°/4000 atm according to the equation

$$PF_3 + SF_6 \rightarrow PF_5 + SF_4 \qquad (95)$$

Phosphorus trifluoride (69 mg, 0.78 mmol) and sulfur hexafluoride (126 mg, 0.86 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 450°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{RT} \sim \underset{(A)}{-160°} \sim \underset{(B)}{-196°} \qquad (2\ \text{times})$$

The following materials were identified.

A SF_6 (120 mg, 0.82 mmol), SF_4 (4.3 mg, 0.04 mmol) and PF_5 (5.0 mg, 0.04 mmol); infrared[116,79,51] and mass spectra[174] identical with that expected for a mixture of SF_6, SF_4 and PF_5.

B PF_3 (65 mg., 0.74 mmol; 5% reaction based on PF_3 consumed; identified by infrared spectrum[79]; confirmed by mass spectrum[174]).

An additional identical experiment in which similiar quantities of reactants are used resulting in reaction with the same products is summarized in Tables IV and XII.

2. The SF_6 - COS System

a. The Attempted Reaction of Sulfur Hexafluoride and Carbonyl Sulfide at 500°/170 atm.

Summary: It was found that SF_6 and COS did not react at 500°/170 atm.

Table IV

Summary of PF_3 and SF_6 System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion[a] (%)	Reactants (mmol)		Material Out (mmol)				
				PF_3	SF_6	PF_3	SF_6	SF_4	PF_5	S
3000	200	24	-	1.15	1.40	1.15	1.40	-	-	-
3000	300	24	-	1.30	1.08	1.29	1.08	-	-	-
4000	400	24	-	0.88	0.90	0.88	0.90	-	-	-
335	450	24	-	0.75	0.74	0.75	0.74	-	-	-
4000	450	24	5	0.78	0.86	0.74	0.82	0.04	0.04	-
335	485	24	20	0.74	0.76	0.59	0.61	0.15	0.15	-
2000	485	24	100	0.90	0.90	-	0.60	-	0.90	0.30
4000	485	24	100	0.87	0.90	-	0.61	-	0.87	0.29

[a] % of PF_3 consumed

Sulfur hexafluoride (168 mg, 1.15 mmol) and carbonyl sulfide (57 mg, 0.95 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 500°/170 atm for 18 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material could not be separated by trap to trap distillation.

The following materials were identified.

SF_6 (168 mg, 1.15 mmol) and COS (57 mg, 0.95 mmol) 100% recovery; infrared[116,33] and mass spectra identical with that expected for a mixture of SF_6 and COS.

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables V and XIII.

b. The Reaction of Sulfur Hexafluoride and Carbonyl Sulfide at 500°/4000 atm.

Summary: It was found that SF_6 and COS reacted at 500°/4000 atm according to the equation

$$SF_6 + COS \rightarrow SOF_2 + CF_4 + S \qquad (96)$$

Sulfur hexafluoride (234 mg, 1.60 mmol) and carbonyl sulfide (74.4 mg, 1.24 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-145°} \sim \underset{(B)}{-196°} \qquad \text{(2 times)}$$

The following materials were identified.

A SF_6 (53 mg, 0.36 mmol) and SOF_2 (106 mg, 1.24 mmol) infrared[116,155] and mass spectra identical with that expected for a mixture of SF_6 and SOF_2.

B CF_4 (108 mg, 1.23 mmol; 100% reaction based on COS consumed; identified by infrared spectrum[72]; confirmed by mass spectrum[7]).

S (39 gm, 1.2 mmol) was found in the gold tube and a melting point was determined (110° - 111°).

Another experiment with similiar quantities of reactants which resulted in reaction with formation of the same products is summarized in Tables V and XIII.

3. The SF_6 - CS_2 System

a. The Attempted Reaction of Sulfur Hexafluoride and Carbon Disulfide at 430°/4000 atm.

Summary: It was found that SF_6 and CS_2 did not react at 430°/ 4000 atm.

Sulfur hexafluoride (184 mg, 1.26 mmol) and carbon disulfide (82.8 mg, 1.09 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 430°/4000 atm for 18 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\text{RT} \sim \underset{(A)}{-126^\circ} \sim \underset{(B)}{-196^\circ} \qquad \text{(3 times)}$$

The following materials were identified.

A CS_2 (82.8 mg, 1.09 mmol; 100% recovery; identified by infrared spectrum[206]).

B SF_6 (184 mg, 1.26 mmol; 100% recovery; identified by infrared spectrum[116]; confirmed by mass spectrum).

Table V

Summary of SF_6 and COS System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion (%)	Reactants (mmol)		Material Out (mmol)				
				SF_6	COS	SF_6	COS	CF_4	SOF_2	S
4000	300	24	-	1.26	1.26	1.26	1.26	-	-	-
335	450	20	-	0.91	0.90	0.91	0.90	-	-	-
4000	450	18	-	0.91	0.90	0.91	0.90	-	-	-
170	500	18	-	1.15	0.95	1.15	0.95	-	-	-
270	500	18	100[a]	1.17	1.26	-	0.09	1.17	1.17	1.17
4000	500	24	100[b]	1.60	1.24	0.36	-	1.24	1.23	1.24

[a] % of SF_6 consumed

[b] % of COS consumed

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables VI and XIV.

b. The Reaction of Sulfur Hexafluoride and Carbon Disulfide at 485°/4000 atm.

Summary: It was found that SF_6 and CS_2 reacted at 485°/4000 atm according to the equations

$$SF_6 + 2CS_2 \rightarrow (CF_3)_2S_2 + 3S \qquad (97)$$

and

$$(CF_3)_3S_2 \rightarrow (CF_3)_2S + S \qquad (98)$$

Sulfur hexafluoride (112 mg, 0.77 mmol) and carbon disulfide (56 mg, 0.74 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 485°/4000 atm for 18 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-126°} \sim \underset{(B)}{-196°} \qquad \text{(3 times)}$$

The following materials were identified.

A CS_2 (11mg, 0.15 mmol) and $(CF_3)_2S_2$ (12 mg, 0.06 mmol); 80% reaction based on CS_2 consumed; infrared[206,28] and mass spectra identical with that expected for a mixture of CS_2 and $(CF_3)_2S_2$.

B SF_6 (70 mg, 0.48 mmol) and $(CF_3)_2S$ (37 mg, 0.22 mmol); infrared[116,28] and mass[34] spectra identical with that expected for a mixture of SF_6 and $(CF_3)_2S$.

Sulfur (35.5 mg, 1.11 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

Additional identical experiments in which similiar quantities of reactants were used where reaction occured with the same products are summarized in Tables VI and XIV.

c. The Reaction of Sulfur Hexafluoride and Carbon Disulfide at 520°/270 atm.

Summary: It was found that SF_6 and CS_2 reacted at 520°/270 atm according to the equation

$$2SF_6 + CS_2 \rightarrow CF_4 + 2SF_4 + 2S \qquad (99)$$

Sulfur hexafluoride (185 mg, 1.27 mmol) and carbon disulfide (81.5 mg, 1.07 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 520°/270 atm for 18 hours.

The gold tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{RT} \sim \underset{(A)}{-126°} \sim \underset{(B)}{-145°} \sim \underset{(C)}{-196°}$$

The following materials were identified.

A CS_2 (33 mg, 0.43 mmol; identified by infrared spectrum[206]).

B SF_4 (137 mg, 1.27 mmol; 100% reaction based on SF_6 consumed; identified by infrared spectrum[51]).

C CF_4 (56 mg, 0.64 mmol; identified from infrared spectrum[72]; confirmed by mass spectrum[7]).

Sulfur (40.6 mg, 1.27 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

d. The Reaction of Sulfur Hexafluoride and Carbon Disulfide at 540°/4000 atm.

Summary: It was found that SF_6 and CS_2 reacted at 540°/4000 atm according to the equation

$$3SF_6 + 3CS_2 \rightarrow (CF_3)_2S + CF_4 + 2SF_4 + 6S \qquad (100)$$

Sulfur hexafluoride (142 mg, 0.97 mmol) and carbon disulfide (69 mg, 0.91 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 540°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

RT	-126°	-145°	-196°	(3 times)
	(A)	(B)	(C)	

The following materials were identified.

A $(CF_3)_2S$ (51 mg, 0.30 mmol; identified by infrared spectrum;[28] confirmed by mass spectrum).[34] 100% reaction based on CS_2 consumed.

B SF_6 (8.8 mg, 0.06 mmol) and SF_4 (66 mg, 0.61 mmol); identified from infrared spectrum of the mixture.[116,51]

C CF_4 (26 mg, 0.30 mmol, identified by infrared spectrum[72]).

Sulfur (57.9 mg, 1.81 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

4. The PF_3 - SO_2 System

a. The Attempted Reaction of Phosphorus Trifluoride and Sulfur Dioxide at 25°/3000 atm.

Summary: It was found that PF_3 and SO_2 did not react at 25°/3000 atm.

Phosphorus trifluoride (71 mg, 0.81 mmol) and sulfur dioxide (58 mg, 0.91 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 25°/3000 atm for 30 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

RT ∿ -96° ∿	-126° ∿	-196°	(3 times
	(A)	(B)	

The following materials were identified.

Table VI

Summary of SF_6 and CS_2 System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion (%)	Material In (mmol)		Material Out (mmol)						
				SF_6	CS_2	SF_6	CS_2	$(CF_3)_2S_2$	$(CF_3)_2S$	CF_4	SF_4	S^b
4000	280	18	-	0.65	0.68	0.65	0.68	-	-	-	-	-
4000	430	18	-	1.26	1.09	1.26	1.09	-	-	-	-	-
335	485	24	-	0.87	0.72	0.87	0.72	-	-	-	-	-
1000	485	24	-	0.79	0.75	0.79	0.75	-	-	-	-	-
1350	485	24	19^a	0.75	0.52	0.69	0.42	0.02	0.04	-	-	0.17
4000	485	18	80^a	0.77	0.74	0.48	0.15	0.07	0.22	-	-	1.11
4000	495	18	90^a	0.67	1.53	-	0.15	0.22	0.45	-	-	2.54
170	500	24	-	0.87	0.74	0.87	0.74	-	-	0.64	1.27	-
270	520	18	100^c	1.27	1.07	-	0.43	-	-	0.30	0.61	1.27
4000	540	24	100^a	0.97	0.91	0.06	-	-	0.30			1.81

a % of CS_2 consumed

b calculated for mass balance

c % of SF_6 consumed

A SO_2 (58 mg, 0.90 mmol; 99% recovery; identified by infrared spectrum[184]; confirmed by mass spectrum).

B PF_3 (71 mg, 0.81 mmol; 100% recovery; identified by infrared spectrum[73]; confirmed by mass spectrum[174]).

No solid residue was found in the gold tube.

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables VII and XVI.

b. The Reaction of Phosphorus Trifluoride and Sulfur Dioxide at 130°/4000 atm.

Summary: It was found that PF_3 and SO_2 reacted at 130°/4000 atm according to the equation

$$2PF_3 + SO_2 \rightarrow 2OPF_3 + S \qquad (101)$$

Phosphorus trifluoride (74 mg, 0.84 mmol) and sulfur dioxide (53 mg, 0.83 mmol) were condensed into a gold tube at -196° . The tube was sealed and held at 130°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{RT} \sim \underset{(A)}{-145°} \sim \underset{(B)}{-196°} \qquad \text{(2 times)}$$

The following materials were identified.

A OPF_3 (12 mg, 0.12 mmol) and SO_2 (49 mg, 0.77 mmol); infrared[79] and mass spectra[174] identical with that expected for a mixture of OPF_3 and SO_2.

B PF_3 (63 mg, 0.72 mmol; 14% reaction based on PF_3 consumed; identified by infrared spectrum[79]; confirmed by mass spectrum[174]).

Sulfur was found in the gold tube (∿ 2 mg). The sulfur was collected from several experiments and a melting point was determined (110° - 111°).

Additional identical experiments with similiar quantities of reactants which resulted in reaction to give the same products are summarized in Tables VII and XVI.

c. The Reaction of Phosphorus Trifluoride, Sulfur Dioxide and Sulfur at 200°/4000 atm.

Summary: It was found that PF_3 and SO_2 reacted in the presence of S at 200°/4000 atm according to the equation

$$2PF_3 + SO_2 \rightarrow 2OPF_3 + S \qquad (102)$$

Phosphorus trifluoride (55 mg, 0.63 mmol) and sulfur dioxide (43 mg, 0.67 mmol) were condensed into a gold tube that had been charged with sulfur (100 mg, 3.13 mmol). The tube was sealed and held at 200°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-145°} \sim \underset{(B)}{-196°} \qquad \text{(2 times)}$$

The following materials were identified.

A OPF_3 (37 mg, 0.36 mmol) and SO_2 (31 mg, 0.49 mmol) infrared[79,184] and mass spectra[174] identical with that expected for a mixture of OPF_3 and SO_2.

B PF_3 (24 mg, 0.27 mmol; 57% reaction based on PF_3 consumed; identified by infrared spectrum[79]; confirmed by mass spectrum[174]).

Sulfur (105 mg, 3.28 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

5. The PF_3 - H_2S System

Table VII

Summary of PF_3 and SO_2 System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion[a] (%)	Reactants (mmol)		Material Out (mmol)			
				PF_3	SO_2	PF_3	SO_2	OPF_3	S[b]
3000	25	30	-	0.81	0.91	0.81	0.90	-	-
4000	25	24	-	0.87	0.87	0.86	0.85	-	-
4000	100	24	-	0.81	0.75	0.80	0.78	-	-
2000	130	24	-	0.81	0.82	0.80	0.80	-	-
335	150	24	-	0.84	0.85	0.83	0.83	-	-
4000	130	24	14	0.84	0.83	0.72	0.77	0.12	0.06
3000	130	24	14	0.83	0.84	0.71	0.78	0.12	0.06
670	150	24	4	0.91	0.89	0.87	0.87	0.04	0.02
1350	150	24	10	0.87	0.85	0.78	0.82	0.09	0.05
4000	150	24	84	0.83	0.84	0.13	0.49	0.70	0.35
335	200	24	6	0.82	0.82	0.77	0.80	0.05	0.03
2670	200	24	80	1.13	0.90	0.23	0.45	0.90	0.45
4000	200	24	88	0.82	0.86	0.10	0.50	0.72	0.36
4000	500	30	95	0.81	1.12	0.04	0.74	0.77	0.38

a. % based on mmols of PF_3 consumed.

b. calculated for material balance.

a. The Attempted Reaction of Phosphorus Trifluoride and Hydrogen Sulfide at 100°/4000 atm.

Summary: It was found that PF_3 and H_2S did not react at 100°/4000 atm.

Phosphorus trifluoride (70 mg, 0.80 mmol) and hydrogen sulfide (28 mg, 0.83 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 100°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. No noncondensible material was observed. The mixture was separated as follows

$$\underset{}{\mathrm{RT}} \sim \underset{(A)}{-161^\circ} \sim \underset{(B)}{-196^\circ} \qquad \text{(2 times)}$$

The following were identified.

A H_2S (28 mg, 0.83 mmol; 100% recovery; identified by infrared[4] spectrum).

B PF_3 (70 mg, 0.80 mmol; 100% recovery; identified by infrared spectrum)[79].

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables VIII and XVII.

b. The Reaction of Phosphorus Trifluoride and Hydrogen Sulfide at 200°/4000 atm.

Summary: It was found that PF_3 and H_2S reacted at 200°/4000 atm according to the equation

$$PF_3 + H_2S \rightarrow SPF_3 + H_2 \qquad (103)$$

Phosphorus trifluoride (66 mg, 0.75 mmol) and hydrogen sulfide (26 mg, 0.77 mmol) were condensed into a gold tube at -196°. The

tube was sealed and held at 200°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. About 15 mm of noncondensible gas was observed, then pmumped away. The mixture was separated as follows

RT ∿ -161° ∿ -196° (2 times)
(A) (B)

The following materials were identified.

A SPF_3 (34 mg, 0.28 mmol) and H_2S (17 mg, 0.49 mmol); infrared[39] and mass spectra[107] identical with that expected for a mixture of SPF_3 and H_2S.

B PF_3 (41 mg, 0.47 mmol; 37% reaction based on PF_3 consumed; identified by infrared[79] and mass spectra)[174].

Additional identical experiments with similiar quantities of reactants which resulted in reaction to give the same products are summarized in Tables VIII and XVII.

6. The PF_3 - COS System

a. The Attempted Reaction of Phosphorus Trifluoride and Carbonyl Sulfide at 220°/4000 atm.

Summary: It was found that PF_3 and COS did not react at 220°/4000 atm.

Phosphorus trifluoride (74 mg, 0.84 mmol) and carbonyl sulfide (52 mg, 0.87 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 220°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated according to the following

RT ∿ -160° ∿ -196° (3 times)
(A) (B)

Table VIII

Summary of PF_3 and H_2S System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion[a] (%)	Reactants (mmol) PF_3	H_2S	Material Out (mmol) PF_3	H_2S	SPF_3	H_2[b]
1670	25	72	-	1.70	1.05	1.69	1.04	-	-
4000	100	24	-	0.80	0.83	0.80	0.83	-	-
2000	150	24	-	0.66	0.65	0.65	0.64	-	-
670	200	24	-	0.92	0.91	0.92	0.91	-	-
4000	150	24	3	0.74	0.78	0.72	0.76	0.02	0.02
1350	200	24	3	0.87	0.84	0.85	0.81	0.03	0.03
4000	200	24	37	0.75	0.77	0.57	0.49	0.28	0.28
2800	300	20	48	1.24	1.59	0.64	0.99	0.60	0.60
670	500	20	31	1.11	1.19	0.77	0.85	0.34	0.34
3300	500	18	41	0.86	0.87	0.51	0.52	0.35	0.35

a. % based on mmols PF_3 consumed.

b. calculated for material balance.

The following material were identified.

A COS (52 mg, 0.87 mmol; 100% recovery; identified by infrared spectrum[33]).

B PF_3 (74 mg, 0.84 mmol; 100% recovery; identified by infrared spectrum[79]).

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables IX and XVIII.

b. The Reaction of Phosphorus Trifluoride and Carbonyl Sulfide at 260°/4000 atm.

Summary: It was found that PF_3 and COS reacted at 260°/4000 atm according to the equation.

$$PF_3 + COS \rightarrow SPF_3 + CO \qquad (104)$$

Phosphorus trifluoride (67 mg, 0.76 mmol) and carbonyl sulfide (51 mg, 0.85 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 260°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. About 3 mm of a noncondensible gas was observed. The volatile material was separated according to the following

$$\text{RT} \sim \underset{(A)}{-160°} \sim \underset{(B)}{-196°} \qquad \text{(3 times)}$$

The following materials were identified.

A COS (48 mg, 0.80 mmol) and SPF_3 (6 mg, 0.05 mmol); infrared[33,39] and mass[107] spectra identical with that expected for a mixture of COS and SPF_3.

B PF_3 (62 mg, 0.71 mmol; 7% reaction based on PF_3 consumed; identified by infrared spectrum[79]; confirmed by mass spectrum[174]).

CO (1.4 mg, 0.05 mmol; identified from infrared spectrum[169] of noncondensible phase from other similiar experiments with greater yield).

Additional identical experiments with similiar quantities of reactants resulting in reaction to give the same products are summarized in Tables IX and XVIII.

c. The Reaction of Phosphorus Trifluoride and Carbonyl Sulfide at 300°/3000 atm.

Summary: It was found that PF_3 and COS reacted at 300°/3000 atm according to the equation

$$3PF_3 + 3COS \rightarrow 2OPF_3 + SPF_3 + CS_2 + CO + C \qquad (105)$$

Phosphorus trifluoride (70 mg, 0.80 mmol) and carbonyl sulfide (51 mg, 0.85 mmol were condensed into a gold tube at -196°. The tube was sealed and held at 300°/3000 atm for 24 hours.

The tube was opened and the volatile material was condensed at -196°. About 0.15 mmol of noncondensible gas was also observed. The volatile material was separated as follows

$$\text{RT} \sim \underset{(A)}{-96°} \sim \underset{(B)}{-126°} \sim \underset{(C)}{-160°} \sim \underset{(D)}{-196°} \qquad \text{(3 times)}$$

The following materials were identified.

A CS_2 (11 mg, 0.15 mmol; identified by infrared spectrum[206]).

B OPF_3 (30 mg, 0.29 mmol; identified by infrared spectrum[79]; confirmed by mass spectrum).

C COS (25 mg, 0.41 mmol) and SPF_3 (18 mg, 0.15 mmol); infrared[33,39] and mass spectra[107] identical with that expected for a mixture of COS and SPF_3.

D PF_3 (32 mg, 0.36 mmol, 55% reaction based on PF_3 consumed; identified by infrared spectrum[79]; confirmed by mass spectrum.[174]

CO (4 mg, 0.15 mmol; identified from infrared spectrum[169] of the noncondensible gas).

C (2 mg, 0.15 mmol) was found in the gold tube.

Additional identical experiments with similiar quantities of reactants which resulted in reaction to give the same products are summarized in Tables IX and XVIII.

7. The PF_3 - CS_2 System

a. The Attempted Reaction of Phosphorus Trifluoride and Carbon Disulfide at 25°/4000 atm.

Summary: It was found that PF_3 and CS_2 did not react at 25°/4000 atm.

Phosphorus trifluoride (98.5 mg, 1.12 mmol) and carbon disulfide (78.4 mg, 1.03 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 25°/4000 atm for 18 hours.

The gold tube was opened and the volatile material was trapped at -196°. The volatile material was seperated as follows

$$\text{RT} \sim \underset{(A)}{-126°} \sim \underset{(B)}{-196°} \qquad \text{(3 times)}$$

The following materials were recovered.

A CS_2 (78.4 mg, 1.03 mmol; 100% recovery; identified by infrared spectrum[206]).

B PF_3 (98.4 mg, 1.12 mmol; 100% recovery; identified by infrared spectrum[79]).

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables X and XIX.

b. The Reaction of Phosphorus Trifluoride and Carbon

Table IX

Summary of PF_3 and COS System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion[a] (%)	Reactants (mmol)		Material Out (mmol)						
				PF_3	COS	PF_3	COS	SPF_3	CO[b]	OPF_3	CS_2	C[b]
4000	25	18	-	0.95	1.09	0.05	1.09	-	-	-	-	-
335	150	24	-	1.10	0.92	1.10	0.92	-	-	-	-	-
270	220	24	-	0.82	0.81	0.82	0.81	-	-	-	-	-
4000	220	24	-	0.84	0.87	0.84	0.87	-	-	-	-	-
335	260	24	-	0.78	0.74	0.78	0.74	-	-	-	-	-
670	260	24	1	0.79	0.82	0.78	0.81	0.01	0.01	-	-	-
4000	260	24	7	0.76	0.85	0.71	0.80	0.05	0.05	-	-	-
135	300	24	6	0.72	0.72	0.68	0.68	0.04	0.04	-	-	-
270	300	24	5	0.88	0.87	0.84	0.83	0.04	0.04	-	-	-
540	300	20	23	0.77	1.24	0.59	1.05	0.18	0.18	-	-	-
3000	300	24	55	0.80	0.85	0.36	0.41	0.15	0.15	0.29	0.15	0.15
4000	300	24	27	0.77	9.75	0.56	0.54	0.07	0.07	0.15	0.07	0.07
4000	400	24	52	0.87	0.87	0.42	0.42	0.14	0.14	0.28	0.14	0.17
335	500	20	55	1.00	0.98	0.45	0.43	0.18	0.18	0.37	0.15	0.22
3000	500	24	50	0.84	1.12	0.42	0.70	0.12	0.09	0.33	0.12	0.21

a % of PF_3 consumed

b calculated for mass balance

Disulfide at 400°/4000 atm.

Summary: It was found that PF_3 and CS_2 reacted at 400°/4000 atm according to the equation

$$2PF_3 + CS_2 \rightarrow 2SPF_3 + C \qquad (106)$$

Phosphorus trifluoride (76 mg, 0.86 mmol) and carbon disulfide (59 mg, 0.78 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 400°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\begin{array}{ccccccc} RT & \sim & -126° & \sim & -145° & \sim & -196° \\ & & (A) & & (B) & & (C) \end{array}$$

The following materials were identified.

A CS_2 (54 mg, 0.71 mmol; identified by infrared spectrum;[206] confirmed by mass spectrum).

B SPF_3 (16 mg, 0.12 mmol; identified by infrared[39] and mass spectra)[107].

C PF_3 (64 mg, 0.73 mmol; 15% reaction based on PF_3 consumed; identified by infrared[79] and mass spectra).[174]

Carbon (∿ 1 mg) was found in the gold tube.

Additional identical experiments with similiar quantities of reactants that resulted in reaction to give the same products are summarized in Tables X and XIX.

8. The PF_3 - CO_2 System

a. The Attempted Reaction of Phosphorus Trifluoride and Carbon Dioxide at 350°/2670 atm.

Summary: It was found that PF_3 and CO_2 did not react at 350°/2670 atm.

Table X

Summary of PF_3 and CS_2 System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion[a] (%)	Material In (mmol)		Material Out (mmol)			
				PF_3	CS_2	PF_3	CS_2	SPF_3	C[b]
4000	25	18	-	1.12	1.03	1.12	1.03	-	-
335	150	24	-	0.90	0.82	0.90	0,80	-	-
270	220	24	-	0.83	0.78	0.83	0.78	-	-
4000	220	24	-	0.83	0.73	0.81	0.70	-	-
4000	250	24	-	0.79	0.77	0.79	0.74	-	-
4000	290	24	-	0.73	0.72	0.73	0.70	-	-
335	300	24	-	0.85	0.87	0.85	0.87	-	-
1000	300	24	-	0.76	0.69	0.75	0.66	-	-
1350	300	24	4	0.80	0.76	0.77	0.74	0.03	0.01
4000	300	18	4	1.12	1.03	0.08	1.01	0.04	0.02
4000	400	24	15	0.86	0.78	0.73	0.71	0.13	0.06
670	500	24	53	1.38	1.17	0.65	0.80	0.73	0.36
4000	500	18	70	1.24	1.04	0.37	0.60	0.87	0.43

a % based on PF_3 consumed

b calculated for mass balance

Phosphorus trifluoride (106 mg, 1.20 mmol) and carbon dioxide (68.2 mg, 1.55 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 350°/2670 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The mixture was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-161^\circ} \sim \underset{(B)}{-196^\circ}$$

The following materials were identified.

A CO_2 (68.2 mg, 1.55 mmol; 100% recovery; identified by infrared spectrum).[169]

B PF_3 (106 mg, 1.20 mmol; 100% recovery; identified by infrared spectrum).[79]

Additional identical experiments with similiar quantities of reactants which resulted in no reaction are summarized in Tables XI and XX.

b. The Reaction of Phosphorus Trifluoride and Carbon Dioxide at 400°/4000 atm.

Summary: It was found that PF_3 and CO_2 reacted at 400°/4000 atm according to the equation

$$PF_3 + CO_2 \rightarrow OPF_3 + CO \qquad (107)$$

Phosphorus trifluoride (98 mg, 1.11 mmol) and carbon dioxide (47 mg, 1.07 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 400°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. A noncondensible gas was observed, measured and an infrared spectrum taken. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-126^\circ} \sim \underset{(B)}{-161^\circ} \sim \underset{(C)}{-196^\circ} \qquad \text{(3 times)}$$

The following materials were identified.

A OPF_3 (48 mg, 0.46 mmol; identified by infrared spectrum[79]; confirmed by mass spectrum).[174]

B CO_2 (27 mg, 0.62 mmol; identified by infrared spectrum).[169]

C PF_3 (57 mg, 0.65 mmol; 41% reaction based on PF_3 consumed; identified by infrared[79] and mass spectra).[174]

CO (0.46 mmol; identified from infrared spectrum[169] of noncondensible phase).

Additional identical experiments with similiar quantities of starting materials that resulted in reaction to give the same products are summarized in Tables XI and XX.

c. The Reaction of Phosphorus Trifluoride and Carbon Dioxide at 500°/4000 atm.

Summary: It was found that PF_3 and CO_2 reacted at 500°/4000 atm according to the two equations

$$PF_3 + CO_2 \rightarrow OPF_3 + CO \qquad (108)$$

$$PF_3 + CO \rightarrow OPF_3 + C \qquad (109)$$

Phosphorus trifluoride (97.6 mg, 1.11 mmol) and carbon dioxide (54.1 mg, 1.23 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. A noncondensible gas was observed, measured and an infrared spectrum taken. The volatile material was separated as follows

$$\begin{array}{ccccccc} RT & \sim & -126° & \sim & -161° & \sim & -196° \\ & & (A) & & (B) & & (C) \end{array}$$

The following materials were identified.

A OPF_3 (107 mg, 1.03 mmol; identified by infrared spectrum[79];

by infrared spectrum[79]).

CO (∿ 0.79 mmol; identified from infrared spectrum[169] of the non condensible phase).

C (∿ 2 mg) was found in the gold tube.

9. Miscellaneous Supporting Reactions

a. The Attempted Reaction of Sulfur Hexafluoride and Carbon Dioxide at 500°/4000 atm.

Summary: It was found that SF_6 and CO_2 did not react at 500°/4000 atm.

Sulfur hexafluoride (134 mg, 0.92 mmol) and carbon dioxide (40 mg, 0.84 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 500°/4000 atm for 18 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material could not be separated by trap - to trap distillation

The following materials were identified.

SF_6 (134 mg, 0.92 mmol) and CO_2 (40 mg, 0.84 mmol); 100% recovery; infrared[116,169] and mass spectra identical with that expected for a mixture of SF_6 and CO_2.

b. The Attempted Reaction of Sulfur Hexafluoride and Carbon Monoxide at 500°/4000 atm.

Summary: It was found that SF_6 and CO did not react at 500°/4000 atm.

Sulfur hexafluoride (130 mg, 0.89 mmol) and carbon monoxide (at 45 cm pressure) were condensed into a gold tube at -196°. The

Table XI

Summary of PF_3 and CO_2 System

Pressure (atm)	Temperature (°C)	Time (hr)	Conversion[a] (%)	Material In (mmol) PF_3	Material In (mmol) CO_2	Material Out (mmol) PF_3	Material Out (mmol) CO_2	Material Out (mmol) OPF_3	Material Out (mmol) CO[b]	C[b]
2670	300	24	-	1.20	1.55	1.20	1.55	-	-	-
335	350	24	-	0.97	1.05	0.97	1.05	-	-	-
4000	350	24	-	1.10	1.10	1.10	1.08	-	-	-
335	400	24	-	1.04	1.05	1.04	1.04	-	-	-
670	400	24	-	1.08	1.15	1.07	1.12	-	-	-
1000	400	24	12	0.97	1.03	0.85	0.91	0.12	0.12	-
1350	400	24	11	1.05	1.05	0.93	0.94	0.11	0.11	-
4000	400	24	41	1.11	1.07	0.65	0.62	0.46	0.46	-
335	500	12	71	0.92	0.94	0.27	0.29	0.65	0.64	0.01
4000	500	24	93	1.11	1.23	0.08	0.34	1.03	0.75	0.14

a % based on PF_3 consumed

b calculated for mass balance

tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. About 60 mm of noncondensible gas was observed, measured and an infrared spectrum was taken.

The following materials were identified.

SF_6 (129 mg, 0.89 mg; 99% recovery; identified by infrared spectrum;[116] confirmed by mass spectrum).

CO ($\sim$ 0.41 mmol; identified from infrared spectrum[169] of the non-condensible gas).

c. The Reaction of Sulfur Hexafluoride, Carbon Monoxide and Sulfur at 500°/4000 atm.

Summary: It was found that SF_6, CO and S reacted at 500°/4000 atm according to the equation

$$SF_6 + 5CO + S \rightarrow 3COF_2 + 2COS \qquad (111)$$

Sulfur hexafluoride (127 mg, 0.870 mmol) was condensed into a gold tube that had been charged with sulfur (100 mg, 3.13 mmol). Carbon monoxide (at 45 cm pressure) was then condensed into the tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. About 86 mm of noncondensible gas was also observed, measured and an infrared spectrum taken. The mixture could not be separated by trap to trap distillation.

The following materials were identified.

SF_6 (85 mg, 0.58 mmol), COF_2 (57 mg, 0.87 mmol) and COS (35 mg, 0.58 mmol); 33% reaction based on SF_6 consumed; infrared[116,152,33] and mass spectra identical with that expected for a mixture of SF_6, COF_2

and COS.

CO (∿ 0.57 mmol; identified from infrared spectrum[169] of the non-condensible gas).

d. The Attempted Reaction of Sulfur Hexafluoride, Carbonyl Fluoride and Carbonyl Sulfide at 500°/4000 atm.

Summary: It was found that SF_6, COF_2 and COS did not react at 500°/4000 atm.

A mixture of sulfur hexafluoride, carbonyl fluoride and carbonyl sulfide (85 mg, 0.97 mmol) obtained in a previous experiment was condensed into a gold tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The gold tube was opened and the volatile material was trapped at -196°. The mixture could not be separated by trap to trap distillation.

The following materials were identified.

SF_6, COF_2 and COS (85 mg, 0.97 mmol; 100% recovery; infrared spectrum [152,116,33] identical with one taken on the mixture before reaction).

No reaction was observed in another identical experiment where excess SF_6 (139 mg, 0.95 mmol) was added to the above mixture.

e. The Attempted Reaction of Carbon Disulfide and Carbon Tetrafluoride at 500°/4000 atm.

Summary: It was found that CS_2 and CF_4 did not react at 500°/4000 atm.

Carbon disulfide (52 mg, 0.68 mmol) and carbon tetrafluoride (70 mg, 0.80 mmol) were condensed into a gold tube at -196°. The

tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

RT -131° -196° (2 times)
(A) (B)

The following materials were identified.

A CS_2 (35 mg, 0.46 mmol; 68% recovery; identified by infrared spectrum[206]).

B CF_4 (70 mg, 0.80 mmol; 100% recovery; identified by infrared spectrum[72]).

Carbon (∿ 3 mg, 0.22 mmol) and Sulfur (14 mg, 0.44 mmol) were found in the gold tube due to decomposition of CS_2.

f. The Attempted Reaction of Carbon Disulfide and Carbon Dioxide at 450°/4000 atm.

Summary: It was found that CS_2 and CO_2 did not react at 450°/4000 atm.

Carbon disulfide (75 mg, 0.99 mmol) and carbon dioxide (53 mg, 1.21 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 450°/4000 atm for 18 hours.

The tube was opened and the volatile material was separated as follows

RT ∿ -131° ∿ -196° (2 times)
(A) (B)

The following materials were identified

A CS_2 (75 mg, 0.99 mmol; 100% recovery; identified by infrared spectrum[206]).

B CO_2 (53 mg, 1.21 mmol; 100% recovery; identified by infrared spectrum[169]).

g. The Attempted Reaction of Carbon Disulfide and Carbonyl Sulfide at 500°/4000 atm.

Summary: It was found that CS_2 and COS did not react at 500°/4000 atm.

Carbon disulfide (85 mg, 1.12 mmol) and carbonyl sulfide (76 mg, 1.27 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was condensed into a gold tube at -196°. The volatile material was separated as follows

$$\text{RT} \sim \underset{(A)}{-131°} \sim \underset{(B)}{-196°} \qquad \text{(2 times)}$$

The following materials were identified.

A CS_2 (85 mg, 1.12 mmol; 100% recovery; identified by infrared spectrum[206]).

B COS (76 mg, 1.27 mmol; 100% recovery; identified by infrared spectrum[33]).

h. The Attempted Decomposition of Carbonyl Sulfide at 500°/4000 atm.

Summary: It was found that COS did not undergo thermal decomposition at 500°/4000 atm.

Carbonyl sulfide (61 mg, 1.02 mmol) was condensed into a gold tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°.

The following material was identified.

COS (61 mg, 1.02 mmol; 100% recovery; identified by infrared spectrum[33]).

No decomposition of COS was observed in additional identical experiments at 500°/170 atm and 500°/270 atm in which similar quantities of COS were reacted for 24 hour periods.

i. The Attempted Decomposition of Carbon Disulfide at 250°/4000 atm.

Summary: It was found that CS_2 did not decompose at 250°/4000 atm.

Carbon disulfide (86 mg, 1.13 mmol) was condensed into a gold tube at -196°. The tube was sealed and held at 250°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°.

The following material was identified.

CS_2 (84 mg, 1.11 mmol; 98% recovery; identified by infrared spectrum).[206]

j. The Decomposition of Carbon Disulfide at 500°/270 atm.

Summary: It was found that CS_2 decomposed at 500°/270 atm according to the equation

$$CS_2 \rightarrow C + 2S \qquad (112)$$

Carbon disulfide (83 mg, 1.09 mmol) was condensed into a gold tube at -196°. The tube was sealed and held at 500°/270 atm for 24 hours.

The tube was opened and the volatile material was trapped at

-196°.

The following materials were identified.

CS_2 (40 mg, 0.53 mmol; 49% recovery; identified by infrared spectrum[206]). Carbon (7 mg, 0.56 mmol) and sulfur (26 mg, 1.12 mmol; mp. 110° - 111°) were found in the gold tube.

In an identical experiment at 500°/4000 atm, CS_2 was found to decompose to C and S with 40% reaction.

k. The Decomposition of Bisperfluoromethyl Disulfide

Summary: It was found that $(CF_3)_2S_2$ decomposed at 500°/ autogenous pressure according to the equation

$$(CF_3)_2S_2 \rightarrow (CF_3)_2S + S \qquad (113)$$

Bisperfluoromethyl disulfide (408 mg, 2.02 mmol) was condensed into a microreactor at -196°. The reactor was closed and heated at 500° for 24 hours.

The reactor was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-96°} \sim \underset{(B)}{-196°}$$

A $(CF_3)_2S_2$ (36 mg, 0.18 mmol; 91% reaction based on $(CF_3)_2S_2$ consumed, identified by infrared spectrum[28]; confirmed by mass spectrum[34]).

B $(CF_3)_2S$ (313 mg, 1.84 mmol, identified by infrared spectrum[28]; confirmed by mass spectrum[34]).

Sulfur (59 mg, 1.84 mmol was recovered from the microreactor and a melting point, 110° - 111°, determined).

l. The Attempted Reaction of Carbon and Carbon Tetrafluoride at 500°/4000 atm.

Summary: It was found that C and CF_4 did not react at 500°/

4000 atm.

Carbon tetrafluoride (84 mg, 0.95 mmol) was condensed into a gold tube at -196° that had been charged with carbon (100 mg, 8.22 mmol). The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°.

The following materials were identified.

CF_4 (84 mg, 0.95 mmol; 100% recovery; identified by infrared spectrum;[72] confirmed by mass spectrum[7]).

Carbon (100 mg, 8.33 mmol) was recovered from the gold tube.

m. The Attempted Reaction of Sulfur and Carbon Tetrafluoride at 500°/4000 atm.

Summary: It was found that S and CF_4 did not react at 500°/4000 atm.

Carbon tetrafluoride (107 mg, 1.22 mmol) was condensed into a gold tube at -196° that had been charged with sulfur (200 mg, 6.25 mmol). The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°.

The following materials were identified.

CF_4 (107 mg, 1.22 mmol; 100% recovery; identified by infrared spectrum;[72] confirmed by mass spectrum[7]).

Sulfur (200 mg, 6.25 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

n. The Attempted Reaction of Sulfur and Sulfur Hexa-

fluoride at 500°/4000 atm.

Summary: It was found that S and SF_6 did not react at 500°/ 4000 atm.

Sulfur (100 mg, 3.13 mmol) was loaded into a gold tube. Sulfur hexafluoride (142 mg, 0.97 mmol) was condensed into the tube at -196°. The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material trapped at -196°. The following materials were identified.

SF_6 (142 mg, 0.97 mmol; 100% recovery; identified by infrared spectrum;[116] confirmed by mass spectrum).

Sulfur (100 mg, 3.13 mmol) was recovered from the gold tube and a melting point degermined (110° - 111°).

o. The Reaction of Bisperfluoromethyl Disulfide and Carbon Disulfide at 540°/4000 atm.

Summary: It was found that $(CF_3)_2S_2$ and CS_2 reacted at 540°/ 4000 atm according to the equation

$$(CF_3)_2S_2 + CS_2 \rightarrow C_nF_{2n+2} + C + S \qquad (114)$$

$$(n = 1, 2, 3, 4, 5)$$

Bisperfluoromethyl disulfide (168 mg, 0.832 mmol) and carbon disulfide (61 mg, 0.80 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 540°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\begin{array}{ccccccc} RT & \sim & -96° & \sim & -145° & \sim & -196° \\ & (A) & & (B) & & (C) & \end{array}$$

The following materials were identified

A CS_2, $(CF_3)_2S_2$, C_5F_{12} and C_4F_{10} (identified from infrared[206,28] and mass[7,34] spectra of the mixture).

B $(CF_3)_2S$, C_3F_8 and C_2F_6 (identified from the infrared[28] and mass[7] spectra of the mixture).

C CF_4 (18 mg, 0.20 mmol; identified by infrared spectrum[72]; confirmed by mass spectrum[7]).

A mixture of carbon and sulfur was found in the gold tube.

p. The Reaction of Carbon Disulfide and Sulfonyl Fluoride at 540°/4000 atm.

Summary: It was found that CS_2 and SOF_2 reacted at 540°/4000 atm according to the equation

$$8CS_2 + 5SOF_2 \rightarrow CF_4 + 5COS + (CF_3)_2S + 15S \qquad (115)$$

Carbon disulfide (68 mg, 0.90 mmol) and sulfonyl fluoride (41 mg, 0.48 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 540°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{RT} \sim \underset{(A)}{-96°} \sim \underset{(B)}{-130°} \sim \underset{(C)}{-196°}$$

The following materials were identified.

A CS_2 (10 mg, 0.13 mmol; identified by infrared spectrum[206]).

B $(CF_3)_2S$ (17 mg, 0.10 mmol; identified by infrared spectrum[28]).

C COS (28 mg, 0.47 mmol) and CF (9mg; 0.10 mmol); identified by infrared spectrum[33,51] of the mixture.

Sulfur (44 mg, 1.38 mmol; mp 110° - 111°) was recovered from the gold tube.

q. The Reaction of Carbon and Sulfur Hexafluoride

at 500°/4000 atm.

Summary: It was found that SF_6 and C reacted at 500°/4000 atm according to the equation

$$C + 2SF_6 \rightarrow CF_4 + 2SF_4 \qquad (116)$$

Sulfur hexafluoride (150 mg, 1.03 mmol) was condensed into a gold tube which had been charged with carbon (60.1 mg, 5.00 mmol). The tube was sealed and held at 500°/4000 atm for 24 hours.

The tube was opened and the volatile material trapped at -196°. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-160°} \sim \underset{(B)}{-196°}$$

The following materials were identified.

A SF_6 (80 mg, 0.55 mmol) and SF_4 (52 mg, 0.48 mmol); infrared spectrum[116,51] identical to that expected for a mixture of SF_6 and SF_4; 47% reaction based on SF_6 consumed.

B CF_4 (21 mg, 0.24 mmol; identified by infrared spectrum.)[72]

Unreacted carbon was found in the gold tube.

r. The Reaction of Bisperfluoromethyl Disulfide and Sulfur Hexafluoride at 540°/4000 atm.

Summary: It was found that $(CF_3)_2S_2$ and SF_6 reacted at 540°/4000 atm according to the equation

$$(CF_3)_2S_2 + 5SF_6 \rightarrow 2CF_4 + 7SF_4 \qquad (117)$$

Bisperfluoromethyl disulfide (162 mg, 0.802 mmol) and sulfur hexafluoride (644 mg, 4.41 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 540°/4000 atm for 24 hours.

The tube was opened and the volatile material was trapped at

-196°. The volatile material was separated as follows

$$\begin{array}{ccccc} RT & \sim & -145° & \sim & -196° \\ & & (A) & & (B) \end{array}$$

The following materials were identified.

A SF_6 (58 mg, 0.40 mmol) and SF_4 (606 mg, 5.61 mmol); infrared[116,51] and mass spectra identical with that expected from a mixture of SF_6 and SF_4.

B CF_4 (141 mg, 1.60 mmol; 100% reaction based on $(CF_3)_2S_2$ consumed; identified by infrared spectrum[72]; confirmed by mass spectrum[7]).

s. The Reaction of Sulfur Dioxide and Thiophosphoryl Fluoride at 150°/4000 atm.

Summary: It was found that SO_2 and SPF_3 reacted at 150°/4000 atm according to the equation

$$SO_2 + 2SPF_3 \rightarrow 2OPF_3 + 3S \tag{118}$$

Sulfur dioxide (51 mg, 0.80 mmol) and thiophosphoryl fluoride (91 mg, 0.76 mmol) were condensed into a gold tube at -196°. The tube was sealed and held at 150°/4000 atm for 24 hours.

The tube was opened and the volatile material was separated as follows

$$\begin{array}{ccccc} RT & \sim & -126° & \sim & -196° \\ & & (A) & & (B) \end{array} \qquad \text{(2 times)}$$

The following materials were identified.

A SO_2 (34 mg, 0.53 mmol) and OPF_3 (56 mg, 0.54 mmol); infrared[184,79] and mass[174] spec-ra identical with that expected for a mixture of SO_2 and OPF_3.

B SPF_3 (26 mg, 0.22 mmol; 71% reaction based on SPF_3 consumed; identified by infrared spectrum[39]; confirmed by mass spectrum[107]).

Sulfur (26 mg, 0.81 mmol) was recovered from the gold tube and a melting point determined (110° - 111°).

t. The Attempted Reaction of Sulfur Dioxide and Thiophosphoryl Fluoride at 170°.

Summary: It was found that SO_2 and SPF_3 did not react at 170° and autogenous pressure.

Sulfur dioxide (132 mg, 2.07 mmol) and thiophosphoryl fluoride (241 mg, 2.01 mmol) were condensed into a glass reactor at -196°. The reactor was closed and heated to 170° in a mineral oil bath for 12 hours.

The reactor was cooled and opened to the vacuum system. The volatile material was trapped at -196°. The volatile material was separated as follows

$$\underset{}{\text{RT}} \sim \underset{(A)}{-130°} \sim \underset{(B)}{-196°} \qquad \text{(2 times)}$$

The following materials were identified.

A SO_2 (132 mg, 2.07 mmol; 100% recovery; identified by infrared spectrum[184]).

B SPF_3 (241 mg, 2.01 mmol; 100% recovery; identified by infrared spectrum[39]).

CHAPTER III

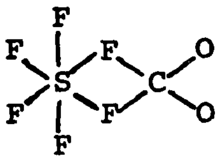
DISCUSSION

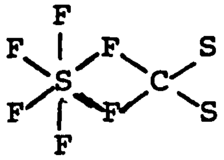
Many of the systems reported here were indeed found to be affected by high pressure as well as by high temperatures in some cases. The minimum temperature/pressure parameters are given along with the products and yields of these reactions. As the temperature and/or pressure were varied, the nature of the products as well as the percentage of reaction varied for some of the systems and these differences are discussed.

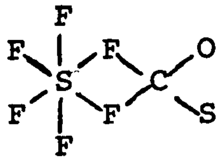
Where possible, reaction pathways have been proposed and supported with experimental and literature evidence. Correlations have been drawn as to the relative reactivities of related systems based on free energy[215] and bond energy[216,217] data.

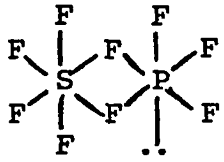
A. Reactions of Sulfur Hexafluoride

The reactions of SF_6 with CO_2, CS_2, COS as well as with PF_3 appear to begin with the formation of a common intermediate. It seems plausible that a transition state complex is initially being formed between one SF_6 molecule and one or two of the other species depending on the pressure/temperature conditions. Such intermediates would involve breaking of the double bonds in CO_2, CS_2 and COS as well as rehybridization of the central atom these molecules from sp to sp^3 hybrids. In PF_3 no bonds are broken but rehybridization occurs from sp^3 to sp^3d^2. From the resulting products that were identified in this research intermediates of the following structures are proposed

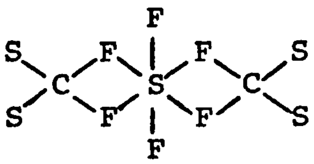


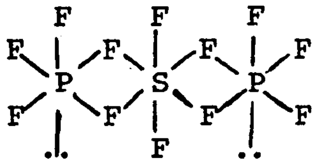






A trimolecular complex could also be possible, for example,





If such complexes could form under conditions of high pressure, then the successful formation of products would be dependent on the cleavage of bonds whose strengths were relatively weak compared to stronger bonds that might be formed in the formation of the complex. For example the formation of C - F bonds or P - F bonds liberate 115.9 kcal/mole and 117.1 Kcal/mole respectively while the breaking of an S - F bond requires only 77.9 K cal/mole.[216] The successful reaction of SF$_6$ with COS, CS$_2$ and CO$_2$ is also dependent on the cleavage of a S or O atom from the initial intermediate that forms. From the experimental evidence it appears that in the case of CO$_2$ either no initial adduct forms with SF$_6$ or if it does adaquate energy is not available to permit the C - O bond to break.

Each of these systems will be discussed individually and certain correlations will be drawn for all of them in a summary.

1. The SF$_6$ - PF$_3$ System. This reaction system was most unusual due to the relative inertness of both species. Unlike PF$_5$

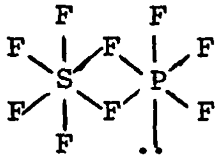
which shows very strong acceptor properties, PF_3 does not show such a tendency and does not form stable adducts at room temperature even with strong organic bases. On the other hand, SbF_3 and AsF_3 do act as acceptors to organic bases. High pressure should certainly favor the formation of complexes with PF_3 in a similiar fashion to that reported for SbF_3 and AsF_3.[142] Even though these complexes might not exist at normal pressures, they could provide a suitable intermediate at high pressures which could lead to stable products.

For the system of SF_6 and PF_3, no reaction was observed at 400°/4000 atm or 450°/335 atm. At conditions of 485°/2000 atm and 485°/4000 atm the PF_3 was totally consumed according to the following reaction

$$3PF_3 + SF_6 \rightarrow 3PF_5 + S \qquad (119)$$

It is proposed that this reaction is taking place through an initial complex between SF_6 and PF_3 like the following

$SF_6 + PF_3 \rightarrow$



(120)

This complex could then decompose by breaking two S - F bonds to give SF_4 + PF_5. The ΔG_r for this reaction at 800°K/1 atm is -51.5 Kcal.[215] The SF_4 that is formed could then react with another mole of PF_3 to give SF_2 and PF_5. The SF_2 which is also a powerful fluorinating agent could react with a third mole of PF_3 giving PF_5 and S. This overall reaction

$$3PF_3 + SF_6 \rightarrow 3PF_5 + S$$

is very energetic with a ΔG_r at 800°K/1 atm of -167.8 Kcal.[215]

The initial proposed complex of SF_6 and PF_3 is similiar to known complexes of group V and group VI compounds like $SbF_5 \cdot SF_4$.[142]

It was observed in this research that at less severe conditions of temperature and/or pressure that SF_4 appeared as a product. At 450°/4000 atm and 485°/335 atm the identified products of the reaction were SF_4 and PF_5. The stoiciometry of this reaction corresponds to a direct reaction between PF_3 and SF_6 like

$$PF_3 + SF_6 \rightarrow PF_5 + SF_4 \qquad (121)$$

but due to the fact that on other occasions at these same conditions PF_5 and S were observed it is believed that the SF_4 was at times formed by the reaction

$$S + 2PF_5 \rightarrow SF_4 + 2PF_3 \qquad (122)$$

These reactions are summarized in Tables IV and XII.

An alternate reaction pathway that has been ruled out involves the prior decomposition of SF_6 via.

$$SF_6 \rightarrow SF_4 + F_2 \qquad (123)$$

The F_2 thus generated could react with the PF_3 to give PF_5 as has similiarly been reported for the reaction of PF_3 with Cl_2[135] or Br_2[133] according to the equations

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2 \qquad (124)$$

$$PF_3 + Br_2 \rightarrow PF_3Br_2 \rightarrow PF_5 + PBr_5 \qquad (125)$$

It is not thought that the SF_6 is decomposing to SF_4 and F_2, however, since the ΔG_r for this reaction at 800°K/1 atm is +79.4 Kcal.[215] Also SF_6 has been reported not to decompose until much higher temperatures.[210] In a variety of other reactions in this research, for example, $S + SF_6$ at 500°/4000 atm and $SF_6 + CO_2$ at 500°/4000 atm no evidence of SF_6 decomposition was ever noted.

2. <u>The SF_6 - COS System</u>. The reactions of SF_6 and COS are

Table XII

Reactions of PF_3 with SF_6

Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
3000	200	-	-
3000	300	-	-
4000	400	-	-
335	450	-	-
4000	450	5	SF_4, PF_5
335	485	20	SF_4, PF_5
2000	485	100	S, PF_5
4000	485	100	S, PF_5

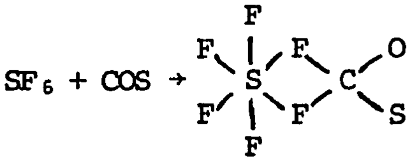
[a] % of PF_3 consumed

summarized in Tables V and XIII. No reaction occured at conditions of 450°/4000 atm or 500°/170 atm. At 500°/270 atm and 500°/4000 atm reaction did occur with total consumption of the limiting reagent to give the same products via.

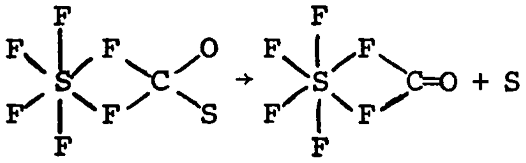
$$SF_6 + COS \rightarrow SOF_2 + CF_4 + S \qquad (126)$$

This reaction took place at lower pressures than analogous SF_6 - CS_2 reactions, 270 atm compared to 1350 atm for CS_2 at about 500°.

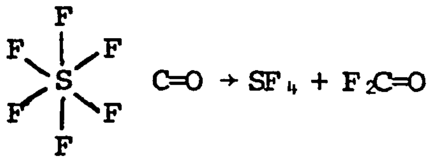
This reaction is postulated to proceed through an intermediate complex, followed by C - S bond cleavage. The overall proposed pathway follows



(127)



(128)



(129)

$$SF_4 + F_2C{=}O \rightarrow SOF_2 + CF_4 \qquad (130)$$

The overall reaction then is

$$SF_6 + COS \rightarrow SOF_2 + CF_4 + S \qquad (131)$$

and has a free energy change ΔG_r at 800°K/1 atm of -40.0 Kcal.[215] The intermediates generated in step (3) are SF_4 and COF_2 are known from the literature to react readily at 500° to give SOF_2 and CF_4 as products[93] with ΔG_r at 800°K/1 atm of -28.4Kcal.[215] It should be noted that the combined reaction of steps (1), (2) and (3) which

Table XIII

Reactions of SF_6 with COS

Pressure (atm)	Temperature (°C)	Conversion (%)	Products
4000	300	-	-
335	450	-	-
4000	450	-	-
170	500	-	-
270	500	100[a]	CF_4, SOF_2, S
4000	500	100[b]	CF_4, SOF_2, S

a % of SF_6 consumed

b % of COS consumed

is

$$SF_6 + COS \rightarrow COF_2 + SF_4 + S \qquad (132)$$

also would occur with a spontaneous ΔG_r of -11.6 Kcal[215] at 800°K/1 atm.

The proposed intermediate COF_2 was not actually observed in the reaction mixture but it was observed in another reaction of SF_6 with CO and S at 500°/4000 atm with a 33% consumption of SF_6 according to the equation

$$SF_6 + 5CO + S \rightarrow 3COF_2 + 2COS \qquad (133)$$

Apparently SF_4 was not formed in this reaction as no SOF_2 was observed in the products of the reaction. It is of interest ot note that SF_6 did not react with either CO or S when they were combined separately at 500°/4000 atm.

Alternate pathways which might be proposed could involve decomposition of SF_6 by

$$SF_6 \rightarrow SF_4 + F_2 \qquad (134)$$

or decomposition of COS[164] by either

$$2COS \rightarrow CO_2 + CS_2 \qquad (135)$$

or

$$COS \rightarrow CO + S \qquad (136)$$

These all seem unlikely since as has been previously argued in (1) SF_6 was never shown to undergo decomposition at the conditions of this work. It was also shown in this work that COS does not decompose up to 500°/4000 atm. Of all the products formed in (2) and (3) only CS_2 has been found to react with SF_6. The other products CO_2, CO and S were found not to react with SF_6 individually and no CO_2 was ever identified in the reaction mixtures. As to the possibility of the CO and S from (3) reacting, it would seem that some COF_2 would have been identified as previously noted.

3. The SF_6 - CS_2 System. The results of the reactions of SF_6 and CS_2 are summarized in Tables VI and XIV. It was found that no reaction took place below 485°/1000 atm and even at 500°/170 atm no reaction was observed. At 485°/1350 atm SF_6 did react with CS_2 according to the equation

$$SF_6 + 2CS_2 \rightarrow (CF_3)_2S_2 + 3S \qquad (137)$$

This reaction is analogous to other fluorinations of CS_2 by compounds like UF_6,[198] IF_5[94] and HgF_2[126] which occur at 25°, 195° and 460° respectively to form $(CF_3)_2S_2$. The compound $(CF_3)_2S$ has also been reported to form between CS_2 and SF_4 in the presence of catalytic amounts of AsF_3 or BF_3 at 200°.[90]

The above reaction also gives $(CF_3)_2S$ as a product which has been shown to be a product of the thermal or photolytic decomposition of $(CF_3)_2S_2$ by the reaction[47,95,117]

$$(CF_3)_2S_2 \xrightarrow[\text{or heat}]{h\nu} (CF_3)_2S + S \qquad (138)$$

The thermal decomposition of $(CF_3)_2S_2$ was reported to begin at 350° and to be 88% complete giving $(CF_3)_2S$ at 400 to 450°.[117] Above 450° the decomposition products were CF_4, C_2F_6, CS_2 and carbonaceous solids.[117]

In this present research, $(CF_3)_2S_2$ was found to decompose only to $(CF_3)_2S$ and S at 500° and autogenous pressure in a metal bomb with 91% conversion of the $(CF_3)_2S_2$. The initial reaction was pressure dependent since at 485°/1350 atm 19% of the SF_6 reacted while at 485°/4000 atm 80% of the SF_6 was consumed. The reaction was also quite temperature dependent as 90% of the SF_6 reacted at conditions of 495°/4000 atm.

In the case of this reaction of SF_6 and CS_2 a trimolecular

Table XIV

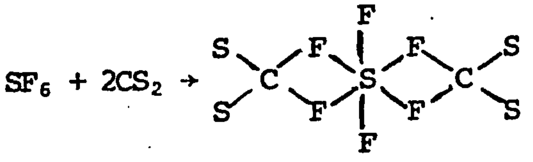
Reactions of SF_6 with CS_2

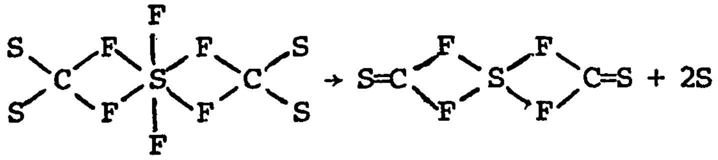
Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
4000	280	-	-
4000	430	-	-
335	485	-	-
1000	485	-	-
1350	485	19	$(CF_3)_2S_2$, $(CF_3)_2S$, S
4000	485	80	$(CF_3)_2S_2$, $(CF_3)_2S$, S
4000	495	90	$(CF_3)_2S_2$, $(CF_3)_2S$, S
170	500	-	-
270	520	100[b]	CF_4, SF_4, S
4000	540	100	$(CF_3)_2S$, CF_4, SF_4, S

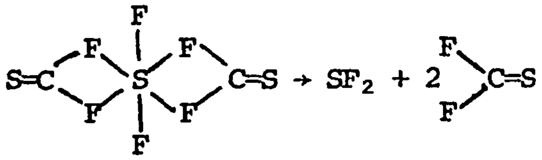
a % of CS_2 consumed

b % of SF_6 consumed

intermediate is proposed as the initiating step for the reaction pathway leads to the formation of the $CF_3S\cdot$ radical which has been proposed in the literature to be a favorable pathway in the formation of $(CF_3)_2S_2$ from IF_5 and CS_2.[27,94] This proposed pathway involves the following steps.


(139)


(140)


(141)

$$SF_2 + 2F_2C{=}S \rightarrow 2F_3C\text{-}S\cdot + S \qquad (142)$$

$$2F_3CS\cdot \rightarrow F_3C\text{-}S\text{-}S\text{-}CF_3 \qquad (143)$$

The net equation then is

$$SF_6 + 2CS_2 \rightarrow (CF_3)_2S_2 + 3S \qquad (144)$$

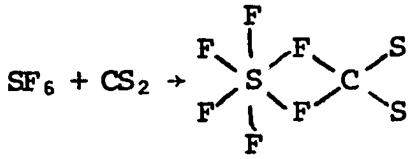
This reaction would indeed be favored by high pressure with a net loss of two moles of gases from reactants to products.

At higher temperatures and lower pressures a different reaction was found to occur between SF_6 and CS_2. At 520°/270 atm the SF_6 was totally consumed according to the equation

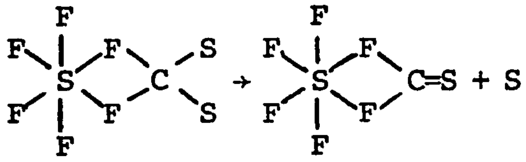
$$2SF_6 + CS_2 \rightarrow 2SF_4 + CF_4 + S \qquad (145)$$

This reaction would not be as dependent on high pressure as the ones producing $(CF_3)_2S_2$. It would appear that high temperature is the overriding factor for this second reaction. The ΔG_r at 800°K/1 atm for this reaction is -28.9 Kcal[215] and it was noted that the reaction becomes more spontaneous at even higher temperatures.

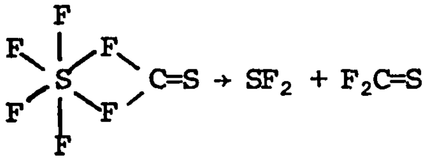
A proposed reaction route for this reaction could also involve an intermediate complex formed between one SF_6 and one CS_2 molecule as is shown in the following sequence.



(146)



(147)



(148)

$$F_2C{=}S + SF_4 \rightarrow SF_4 + CF_4 + S \qquad (149)$$

$$SF_2 + SF_6 \rightarrow 2SF_4 \qquad (150)$$

This series of reactions would yield the net reaction

$$2SF_6 + CS_2 \rightarrow CF_4 + 2SF_4 + 2S \qquad (151)$$

In another reaction at even higher temperature, but also at high pressure, 540°/4000 atm, the following reaction took place between SF_6 and CS_2

$$3SF_6 + 3CS_2 \rightarrow (CF_3)_2S + CF_4 + 2SF_4 + 3S \qquad (152)$$

This reaction appears to be a combination of both of the previously discussed reactions with $(CF_3)_2S$ forming mainly due th the high pressure which favors the formation of $(CF_3)_2S_2$ followed by thermal decomposition to $(CF_3)_2S$ and S. The other products, CF_4 and SF_4 are probably being formed due to high temperature.

An alternate pathway that might be proposed would be the initial decomposition of CS_2 which was found to occur at both 500°/4000 atm, and 500°/270 atm; however, it was noted in this series of reactions, for example at 500°/170 atm, no CS_2 decomposition was observed, possibly because it was stabilized by the SF_6 in some fashion. Carbon disulfide was also observed not to decompose in the presence of other gases, with CO_2 at 450°/4000 atm and with COS at 500°/4000 atm. Still, assuming thermal decomposition of CS_2 as a possibility, the following reactions were attempted at 500°/4000 atm in order to see any correlations in the products formed.

$$S + CF_4 \rightarrow \text{no reaction} \qquad (153)$$

$$S + SF_6 \rightarrow \text{no reaction} \qquad (154)$$

$$C + CF_4 \rightarrow \text{no reaction} \qquad (155)$$

$$C + 2SF_6 \rightarrow CF_4 + 2SF_4 \qquad (156)$$

While this last reaction was found to occur at 500°/4000 atm it still appears unlikely that the decomposition of CS_2 was the initial step since at 495°/4000 atm CS_2 and SF_6 were found to react according to the previously mentioned equation

$$2CS_2 + SF_6 \rightarrow (CF_3)_2S_2 + 3S \qquad (157)$$

Even if the SF_4 reacted furthur with CS_2 to give $(CF_3)_2S_2$, the whereabouts of the CF_4 cannot be explained. Neither were $(CF_3)_2S_2$, $(CF_3)_2S$ nor S found in the products of C and SF_6.

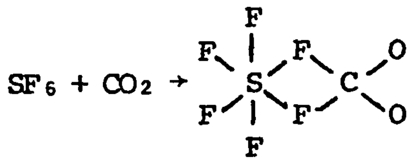
The study of the SF_6 - CS_2 system was continued by investigating the reactions of $(CF_3)_2S_2$ with excess SF_6 or CS_2 at high pressures. It was found that $(CF_3)_2S_2$ and SF_6 did not react at 540°/270 atm although some decomposition of $(CF_3)_2S_2$ to $(CF_3)_2S$ and S did occur. At 540°/4000 atm excess SF_6 with $(CF_3)_2S_2$ reacted consuming all the $(CF_3)_2S_2$ according to the equation

$$(CF_3)_2S_2 + 5SF_6 \rightarrow 2CF_4 + 7SF_4 \qquad (158)$$

It was interesting in this reaction that no free sulfur was found as some certainly must have been formed. Apparently it was fluorinated and resulted in part of the SF_4 that was formed.

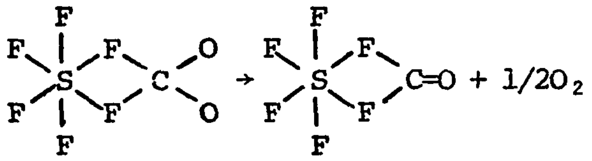
In the presence of excess CS_2 all the $(CF_3)_2S_2$ reacted at 540°/4000 atm giving a mixture of perfluoroalkanes, C_nF_{2n+2} (n = 1 to 5) with carbon and sulfur also being formed.

4. <u>The SF_6 - CO_2 System</u>. During the course of this research, no reaction was ever observed between SF_6 and CO_2. Due to the structural similarity of CO_2 with COS or CS_2 some reaction might be expected since analogous intermediates could be postulated. It appears that the lack of reactivity of SF_6 and CO_2 at 500°/4000 atm is due to either the initial formation of the complex



(159)

where the C=O bonds will not open or in the next step of C-O bond cleavage:



(160)

The energy requirements are certainly greater for breaking a C-O bond (80.3 Kcal)[216] compared to a C-S bond (65.0 Kcal or less)[216] in the COS or CS_2 reactions.[217] If these two steps could proceed in the proposed pathway, it appears that a reaction could occur.

For some net reactions that may be postulated for SF_6 and CO_2, however, they are not feasible, thermodynamically. For example for a reaction similiar to COS

$$SF_6 + CO_2 \rightarrow SOF_2 + CF_4 + O_2 \qquad (161)$$

ΔG_r at 800°K/1 atm is +4.2 Kcal.[215] This overall reaction is not pressure favored, however. If the proposed intermediate could form, giving a negative ΔV^*, this reaction could quite possibly go at 500°/4000 atm.

For another possible reaction similiar to the reaction of SF_6 and CS_2 at 520°/270 atm

$$2SF_6 + CO_2 \rightarrow 2SF_4 + CF_4 + O_2 \qquad (162)$$

the ΔG_r at 800°K/1 atm is +61.84 Kcal[215] which certainly would not be feasible.

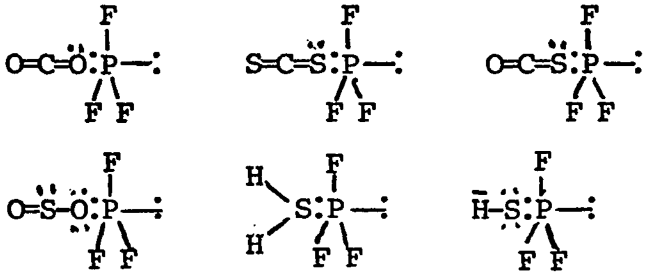
Again this system supports the idea that none of the SF_6 reactions are proceeding through initial SF_6 decomposition since no reaction was observed. If SF_4 and F_2 were formed in this reaction either would react with CO_2 via. known reactions. The reaction of CO_2 and F_2 has been reported to occur at 25° giving $CF_2(OF)_2$ as one product.[37,100] Sulfur tetrafluoride is reported to react readily with CO_2 at 500° to form COF_2 or CF_4 in excess SF_4.[93,4]

5. Summary of SF_6 Reactions. It appears that in each of these reactions with SF_6 that either a bi- or trimolecular intermediate is forming under high pressure except in the case of CO_2. The reactions all appear to occur through coordination of two F atoms to empty hybridized orbitals of PF_3, COS and CS_2 which are acting as acceptors. The reactions with PF_3 seem to be the fastest probably due to the fact that no bonds are broken except S - F bonds in forming intermediates. The COS and CS_2 reactions both involve C - S bond cleavage and from previous evidence it appears that the C - S bond from COS is much

weaker than the C - S bond in CS_2 hence the COS system shows a greater reactivity with larger yields at relatively the same temperatures. The general order of reactivity then may be stated $PF_3 > COS > CS_2 > CO_2$ towards SF_6. Table XV summarizes the correlations for the SF_6 reactions.

B. Reactions of Phosphorus Trifluoride

The reactions of PF_3 with CO_2, CS_2, COS, SO_2 and H_2S are very similiar in that it appears that the initiating step in each reaction involves a bimolecular transition state, a Lewis acid-base adduct, with PF_3 acting as the acceptor and the other molecule acting as a donor. For the compounds noted, the relative reactivities would be dependent on the various bonds being formed and broken. High pressure should favor the formation of such intermediates and increased temperature should favor appropriate bond cleavage proportionate to the initial bond strengths. Possible structures for intermediates of this type are shown below.



After the initial formation of the adduct, bond cleavage occurs forming either OPF_3 or SPF_3 and another specie. Depending on the nature of this other specie it may or may not be possible to identify it in the reaction mixture. Stable molecules like CO or H_2 were identified. On the other hand the formation of highly reactive CS or SO, which would immediately react furthur, were not identified, but only proposed, based on the final products of the reaction.

Table XV

Summary of Correlations for SF_6 Reactions

Acceptor Molecule	Minimum T For Reaction (°C)	Minimum P For Reaction (atm)	P at Minimum T For No Reaction (atm)	ΔG_r (800°K) for Net Reaction (Kcal)	Energy to Break C-S or C-O bond (Kcal/mole)	Energy Liberated in forming P-F or C-F bond (Kcal/mole)
PF_3	450	4000	335	-167.8	none	117.1
COS	500	270	170	- 40.0	< 65.0	115.9
CS_2	485	1350	1000	- 28.9[a]	65.0	115.9
CO_2	none	none	none	+ 4.2[b] + 61.8[c]	80.3	115.9

[a] this value for $2SF_6 + CS_2 \rightarrow 2SF_4 + CF_4 + S$

[b] for analogous COS reaction

[c] for analogous CS_2 reaction

A number of correlations can be drawn to explain the general trend of reactivity of these Lewis bases towards PF_3. One may look at the free energy changes (at 1 atm and minimum temperature conditions for reaction) and observe that the more reactive species produce a greater negative free energy change. It is also of value to correlate the ease of reaction with the ease of breaking a bond from the initial intermediate that has been proposed. For the most part it was found that the strengths of these bonds had a direct relationship to the experimentally determined order of reactivity.

In general the proposed pathway for all of these reactions involves the following steps.

$$\text{(1)}\quad \text{A-B}\colon + PF_3 \rightarrow \text{A-B}\overset{\cdot\cdot}{\colon} PF_3 \qquad \text{(adduct formation)}$$

$$\text{(2)}\quad \text{A-B}\overset{\cdot\cdot}{\colon} PF_3 \rightarrow \text{A} + \text{B}\colon\colon PF_3 \qquad \text{(bond cleavage)}$$

As previously stated the actual presence of (A) was not always verified due to its greater reactivity.

It was found in this research that a trend of reactivity towards PF_3 was established: $SO_2 > H_2S > COS > CS_2 > CO_2$ towards PF_3 based upon minimum temperature/pressure conditions for reaction. In the following discussion each of these systems will by discussed separately, then in summary correlations and generalizations will be made.

1. The PF_3 - SO_2 System. The reaction between PF_3 and SO_2 has been studied by other workers in sealed silica containers with S and traces of SPF_3 and $[F_2(S)P]_2O$ detected as products.[41] This reaction began at 450° and a good yield was obtained at 600°.

In this present research, see Tables VII and XVI, the reaction of PF_3 and SO_2 was found to occur at 130°/2000 or 4000 atm with a 14% conversion of PF_3. The reaction preceeds according to the equation

$$2PF_3 + SO_2 \rightarrow 2OPF_3 + S \qquad (163)$$

The free energy change for this reaction at 400°K (ΔG_r) = -50.9 Kcal.[215] As previously stated, this reaction probably involves an initial adduct formed between SO_2 and PF_3 followed by S-O bond cleavage

$$O{=}\ddot{S}{-}O + \ddot{P}F_3 \rightarrow O{=}\ddot{S}{-}O{:}\ddot{P}F_3 \qquad (164)$$

$$O{=}\ddot{S}{-}O{:}PF_3 \rightarrow SO + OPF_3 \qquad (165)$$

The S=O was not identified but it is known to disproportionate readily <u>via</u>.

$$2SO \rightarrow SO_2 + S \qquad (166)$$

The bond energy of S-O is about 34.9 Kcal/mole[216] so it seems that this cleavage is quite feasible. The S=O formed in step (2) might also react directly with PF_3 forming $OPF_3 + S$ (167)

$$SO + PF_3 \rightarrow SO{:}PF_3 \qquad (168)$$

$$SO{:}PF_3 \rightarrow S + OPF_3 \qquad (169)$$

This reaction is certainly thermodynamically feasible with a ΔG_r = -54.8 Kcal[215] at 400°K. Either of these pathways are supported by the experimental data.

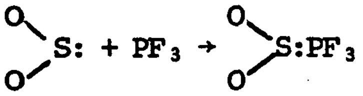
Another possible pathway could involve a prior decomposition of SO_2 but this pathway has been ruled out for a number of reasons. The pathway would involve the reactions

$$SO_2 \rightarrow SO + 1/2O_2 \qquad (170)$$

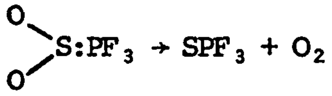
$$1/2O_2 + PF_3 \rightarrow OPF_3 \qquad (171)$$

As in previous arguments the S=O could easily disproportionate gernerating the sulfur found in the reaction. Reaction (1) however would not be pressure favored and also is not energetically favorable with ΔG_r= +65.3[215] Kcal at 400°K. It would also be noted that the reaction (2) would not be quantitative at 400°K so there should be some O_2 present at equilibrium and no noncondensible gas was ever observed in this system.

Another possibility would be for an initial adduct to be formed between SO_2 and PF_3 with bonding occuring through the sulfur



(172)



(173)

$$1/2O_2 + SPF_3 \rightarrow OPF_3 + S \qquad (174)$$

The initial formation of the adduct in (1) would certainly be pressure favored, but again it is noted that no noncondensible gas was noted (O_2). In addition reaction (3) would most likely not be quantitiative and some SPF_3 should be present at equilibrium which was never the case.

The overall reaction was found from the experimental data to be extremely pressure dependent as could be seen by a series of reactions done at 150°. At 150°/335 atm no reaction occured. At 150°/670 atm 4% of the PF_3 was consumed while at 150°/4000 atm 84% of the PF_3 reacted. A 95% conversion of PF_3 was seen at 500°/4000 atm showing some temperature dependence, also.

Both PF_3 and SO_2 may act as either Lewis acids or Lewis bases. Sulfur dioxide acts as an acceptor molecule with a variety of amine bases,[32] oxygen compounds[3] like ethylene oxide or anisol and sulfur compounds like diethylsulfide.[3] It has also been reported to complex with halide ions to give SO_2X^- ions(X = Cl, Br, I).[153] Sulfur dioxide is reported to be a very weak base or donor in a 1:1 complex formed with AsF_5.[31] Phosphorus trifluoride as described in the introduction also acts as an electron pair acceptor or donor depending on its environment. In this present study it would appear that PF_3 is the Lewis acid and SO_2 is the Lewis base with bonding occuring through oxygen rather than sulfur in SO_2.

The postulated formation of S = O is supported by the reported reaction of SO_2 with PCl_3 which has been studied up to 1500°K in which $OPCl_3$ and SO were formed.[188]

It is important to note that SPF_3 was never observed as a product in this reaction although the temperatures and pressures employed were sufficient to form SPF_3 from the reaction of

$$S + PF_3 \rightarrow SPF_3 \qquad (175)$$

Studies of similiar systems in the literature give evidence to why no SPF_3 was observed.

Sulfur dioxide reacts vigorously with $(CH_3)_3P$ at 185° to give the following reaction [190]

$$SO_2 + 2(CH_3)_3P \rightarrow 2(CH_3)_3P{=}O + S \qquad (176)$$

The same workers report that Ph_3P and SO_2 react more slowly at 185° for 3 to 7 days via.

$$3Ph_3P + SO_2 \rightarrow 2Ph_3P{=}O + Ph_3P{=}S \qquad (177)$$

Other workers synthesized a great variety of phosphoryl and thiophosphoryl compounds at 50° and long reaction times using a 10:1 ration of liquid SO_2 to phosphorus compound.[66] The general reaction is

$$3XYZP + SO_2 \rightarrow 2XYZP{=}O + XYZP{=}S \qquad (178)$$

(XYZ = alkyl, aryl, alkoxy, Cl, Br, NCO and NCS)

It was found that for all of these reactions the excess SO_2 would react with XYZP=S according to the equation

$$2XYZP{=}S + SO_2 \rightarrow 2XYZP{=}O + 2S \qquad (179)$$

It appears that even though the thiophosphoryl compound forms, it reacts with excess SO_2 to give the phosphoryl compound and sulfur.

This reaction was checked in this research by synthesizing some SPF_3 by reacting S with PF_3 at 300°/4000 atm. The SPF_3 was condensed

Table XVI

Reactions of PF_3 with SO_2

Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
3000	25	-	-
4000	25	-	-
4000	100	-	-
2000	130	-	-
335	150	-	-
4000	130	14	OPF_3, S
3000	130	14	OPF_3, S
670	150	4	OPF_3, S
1350	150	10	OPF_3, S
4000	150	84	OPF_3, S
335	200	6	OPF_3, S
2670	200	80	OPF_3, S
4000	200	88	OPF_3, S
4000	500	95	OPF_3, S

[a] % of PF_3 consumed

into a glass reactor with SO_2 and no reaction was observed upon heating up to 170° for 12 hours. When the SPF_3 and SO_2 were reacted at 130°/4000 atm or 150°/4000 atm reaction took place with over 70% of the SPF consumed according to the equation

$$2SPF_3 + SO_2 \rightarrow 2OPF_3 + S \qquad (180)$$

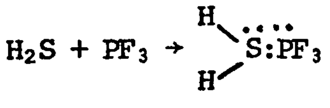
If SPF_3 did form it is likely that it would react with excess SO_2, however, since no trace of SPF_3 was ever seen, it is possible that it does not form at all in the initial reaction of PF_3 and SO_2.

2. The PF_3 - H_2S System. The reaction of PF_3 and H_2S are summarized in Tables VIII and XVII. There was a definite pressure dependence in this system with initial reaction occuring at 150°/4000 atm with 3% conversion of PF_3. The reaction occurred at lower pressures but higher temperatures were needed. At 200°/1350 atm 3% of the PF_3 was consumed while at 200°/4000 atm 37% reaction of PF_3 was noted. At 200°/670 atm no reaction occured which indeed points out the effect of pressure on this system.

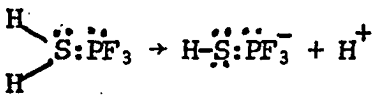
In all cases where reaction did occur the products are the same.

$$PF_3 + H_2S \rightarrow SPF_3 + H_2 \qquad (181)$$

This reaction is energetically favorable with a $\Delta G_r = -28.5\mathrm{Kcal}$[215] at 400°K/1 atm. It appears likely that the reaction pathway for this reaction involves an adduct of possibly one of two types. First it appears that a molecular adduct is being formed between one PF_3 and one H_2S molecule with H_2S acting as the donor and PF_3 the acceptor.



$$H_2S + PF_3 \rightarrow H_2\ddot{S}{:}PF_3 \qquad (182)$$



$$H_2\ddot{S}{:}PF_3 \rightarrow H{-}\ddot{S}{:}PF_3^- + H^+ \qquad (183)$$

Table XVII

Reactions of PF_3 with H_2S

Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
1670	25	-	-
4000	100	-	-
2000	150	-	-
670	200	-	-
4000	150	3	SPF_3, H_2
1350	200	3	SPF_3, H_2
4000	200	37	SPF_3, H_2
2800	300	48	SPF_3, H_2
670	500	31	SPF_3, H_2
3300	500	41	SPF_3, H_2

[a] % of PF_3 consumed

$$H^{+} + \bar{H}\text{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:\ddot{P}F_3 \rightarrow H_2 + SPF_3 \qquad (184)$$

A second reaction route that might be possible involves the autoionization of H_2S under high pressure. It appears that H_2S could undergo autoionization either in the gaseous phase or in a more probable condensed phase. A high pressure study of H_2S in aqueous solution[59] has shown that the degree of ionization increases with increased pressure up to 2000 atm with a ΔV^* of about $-15 cm^3/mole$. This change in volume is proposed to be due to the formation of the ions H_3O^+ and HS^-. There seems to be no additional solvent effects as has been observed for other weak acids like acetic and carbonic acids. This pathway would then involve the following steps.

$$2H_2S \rightarrow H_3S^{+} + SH^{-} \qquad (185)$$

$$SH^{-} + PF_3 \rightarrow \bar{H}SPF_3 \qquad (186)$$

$$H_3S^{+} + H^{-}SPF_3 \rightarrow H_2S + SPF_3 + H_2 \qquad (187)$$

The $\bar{H}SPF_3$ ion that is postulated as an intermediate for either of these pathways has also been postulated in the literature as an intermediate in the reaction of PF_3 with liquid H_2S where the resulting $HPS\bar{F}_3$ ion forms.[44] The possibility of forming an ionic intermediate is known to have a favorable effect on the kinetics[118,207] as was described in the introduction.

As an alternative to having an ionic intermediate, a reaction route could be proposed involving the following steps.

$$H_2S \rightarrow H_2 + S \qquad (188)$$

$$S + PF_3 \rightarrow SPF_3 \qquad (189)$$

This pathway has been ruled out because step (1) which involves bond stretching and cleavage would not be pressure favored.[118] The ΔG_r for step (1) is +8.9 Kcal[215] at 400°K/1 atm and becomes less favorable as temperature increases. Also, as has been pointed out step (2) is not quantitative at 400°K so one would expect some sulfur at equilibrium which was never found. In other experiments H_2S was found to be quite thermally stable up to 500°/4000 atm.

As compared with the reaction of SO_2 and PF_3 it may be noted that the reaction of H_2S and PF_3 occurs at somewhat more vigorous conditions. This may be attributed to the energy requirements for breaking a S-H bond (82.9 Kcal)[216] compared to the S-O bond (34.9 Kcal)[216] in SO_2 after the appropriate adduct with PF_3 has formed.

It appears that an interesting reaction might be proposed to test the formation of the ionic intermediate, $\bar{H}SPF_3$. Possibly PF_3 would react with anhydrous NaHS to yield some SPF_3 and NaH at high pressure via.

$$Na^{+}HS^{-} + PF_3 \rightarrow Na^{+-}HSPF_3 \qquad (190)$$

$$Na^{+-}HSPF_3 \rightarrow NaH + SPF_3 \qquad (191)$$

3. The PF_3 - COS System. The reactions of PF_3 with COS are summarized in Tables IX and XVIII. It was found that the minimum conditions for reaction were 260°/670 atm with only 1% conversion of PF_3 according to the equation

$$PF_3 + COS \rightarrow SPF_3 + CO \qquad (192)$$

At 260°/4000 atm the above reaction occurred with 7% of the PF_3 being consumed. No reaction occurred at conditions of 260°/335 atm or 220°/4000 atm. The free energy change ΔG_r at 500°K for this reaction is -30.4 Kcal[215] at 1 atm. This is very close to the reaction of H_2S in the previous section $\Delta G_r = -28.5$ Kcal.[215] The bond energies are also very close for the C=S bond in COS and the H-S bond in H_2S. The C=S bond has been reported to be 76.9 Kcal[217] while the H-S bond is 82.9 Kcal.[216] From the experimental data it appears that COS will not react with PF_3

except at about 100° higher temperature than H_2S (260° vs 150°). The most probable pathway seems to be the initial formation of a coordinate bond resulting in an adduct under high pressure followed by bond cleavage of the C=S bond according to the following

$$COS + PF_3 \rightarrow O{=}C{=}S{:}\ddot{P}F_3 \tag{193}$$

$$S{=}C{=}S{:}\ddot{P}F_3 \rightarrow C\ O + SPF_3 \tag{194}$$

The chance of an intial adduct forming between the oxygen end of COS with PF_3 and yielding CS + OPF_3 at these conditions would be small. For the reaction

$$PF_3 + COS \rightarrow OPF_3 + CS \tag{195}$$

the ΔG_r at 500°K is +19.1 Kcal.[215] The C=O bond cleavage would not be feasible under these conditions as it is in excess of 199.2 Kcal[217] which is the reported bond energy for C=O in CO_2. It would appear that this reaction does not occur at higher temperatures where OPF_3 is identified as a product. The ΔG_r for the reaction is +19.5 Kcal[215] at 700°K/1 atm. At more rigorous conditions of temperature and pressure a more complex reaction occurs between PF_3 and COS which may be written

$$3COS + 3PF_3 \rightarrow 2OPF_3 + SPF_3 + CO + CS_2 + C \tag{196}$$

This over all reaction is the sum of a number of reactions which are postulated to be

$$3COS + 3PF_3 \rightarrow 3CO + 3SPF_3 \tag{197}$$

$$2CO + 2SPF_3 \rightarrow 2CS + 2OPF_3 \tag{198}$$

$$2CS \rightarrow CS_2 + C \tag{199}$$

ΔG_r at 700°K for the overall reaction is −45.8 Kcal/1 atm[215] and this free energy change should be further enhanced since there is a net loss of one mole of gaseous material at these elevated pressures (3000 to 4000 atm). This reaction was studied at temperatures from 300 to 500° and presures from 335 to 4000 atm with very little change in yield,

Table XVIII

Reactions of PF_3 with COS

Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
4000	25	-	-
335	150	-	-
270	220	-	-
4000	220	-	-
335	260	-	-
670	260	1	SPF_3, CO
4000	260	7	SPF_3, CO
135	300	6	SPF_3, CO
270	300	5	SPF_3, CO
540	300	23	SPF_3, CO
3000	300	55	SPF_3, CO, OPF_3, CS_2, C
4000	300	27	SPF_3, CO, OPF_3, CS_2, C
4000	400	52	SPF_3, CO, OPF_3, CS_2, C
335	500	55	SPF_3, CO, OPF_3, CS_2, C
3000	500	50	SPF_3, CO, OPF_3, CS_2, C

[a] % of PF_3 consumed

usually about 50% conversion of the PF_3.

Reports in the literature state that COS may undergo thermal decomposition via. two independant pathways[164] viz.

$$(1)\quad 2COS \rightleftarrows CO_2 + CS_2 \qquad (200)$$

$$(2)\quad COS \rightleftarrows CO + S \qquad (201)$$

Both of these reactions were ruled out as being possible initiating reactions for the initial formation of SPF_3 and CO by the reaction

$$COS + PF_3 \rightarrow CO + SPF_3 \qquad (202)$$

for the following reasons. For case (1) where the products would be CO_2 and CS_2 it is known from this research that neither of these compounds reacts with PF_3 at 260°/670 atm which was the minimum conditions observed in this reaction. It was found as will be described later in more detail that CS_2 and PF_3 first reacted at 300°/1350 atm and CO_2 and PF_3 first reacted at 400°/1000 atm. In addition no carbon was found which was one of the products formed in the CS_2 reaction. Neither CS_2 nor CO_2 were detected in the reaction. In the second reaction (2) the fact has been pointed out that all of the sulfur would not react with PF_3. Since no sulfur was found at the end to the reaction it may be assumed that the COS is not decomposing to give CO and S. In addition a number of experiments were carried out to attempt to discover if some other than the proposed pathway was occurring. It was observed that COS did not decompose under conditions of high pressure. The COS was recovered quantitatively in a series of attempted decompositions up to 500°/4000 atm. It was also found that $CO_2 + CS_2$ did not react to form COS at 450°/4000 atm. Further, no reaction occurred between COS and CS_2 at 500°/4000 atm.

4. <u>The PF_3 - CS_2 System</u>. The reactions between PF_3 and CS_2

were found to occur with both pressure and temperature dependence. These reactions are summarized in Tables X and XIX. No reaction was observed at 300°/1000 atm or below; however, at 300°/1350 atm and 300°/4000 atm the following reaction took place with a 4% consumption of PF_3.

$$2PF_3 + CS_2 \rightarrow 2SPF_3 + C \qquad (203)$$

This reaction overall is postulated as a two step process. The first step involves the formation of an adduct between CS_2 and PF_3 followed by breaking of a C-S bond.

$$CS_2 + PF_3 \rightarrow S{=}C{=}S{:}PF_3 \qquad (204)$$

$$S{=}C{=}S{:}PF_3 \rightarrow C\ S + SPF_3 \qquad (205)$$

This net reaction

$$CS_2 + PF_3 \rightarrow CS + SPF_3 \qquad (206)$$

has a $\Delta G_r = -10.8$ Kcal[215] at 600°K/1 atm. The CS was not isolated; this is not surprising, due to its very reactive nature. It is thought to react very rapidly with another molecule of PF_3 in a second sequence of reactions

$$C{\equiv}S + PF_3 \rightarrow C{\equiv}S{:}PF_3 \qquad (207)$$

$$C{\equiv}S{:}PF_3 \rightarrow C + SPF_3 \qquad (208)$$

The net reaction here is

$$CS + PF_3 \rightarrow C + SPF_3 \qquad (209)$$

and has a $\Delta G_r = -67.4$ Kcal[215] at 600°K/1 atm.

The breaking of the C=S bond in the first series of reactions helps explain the higher temperature/pressure requirements for this reaction than for the previous system of PF_3 and COS. In both cases a C=S is breaking, but in CS_2 the C=S bond is on the order of 131.7 Kcal[217] while in COS the C=S bond is reported to be 76.9 Kcal.[217] This

Table XIX

Reactions of PF_3 with CS_2

Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
4000	25	-	-
335	150	-	-
270	220	-	-
4000	220	-	-
4000	250	-	-
4000	290	-	-
335	300	-	-
1000	300	-	-
1350	300	4	SPF_3, C
4000	300	4	SPF_3, C
4000	400	15	SPF_3, C
670	500	53	SPF_3, C
4000	500	70	SPF_3, C

---

[a] % of PF_3 consumed

system showed a large temperature dependence as the conversion of PF_3 increased to 15% at 400°/4000 atm. A definite presure dependence was observed at 500° where 53% conversion of PF_3 occurred at 500°/670 atm and this increased to 70% conversion of PF_3 at 500°/4000 atm.

Since CS_2 was shown in separate experiments to decompose thermally to carbon and sulfur it is assumed that a second pathway might be possible involving the decomposition of CS_2 via.

$$CS_2 \rightarrow C + 2S \qquad (210)$$

The sulfur thus formed could then react with the PF_3 giving SPF_3. Since this reaction of S and PF_3 is nearly quantitative at conditions of 300°/4000 atm and above, it can not be completely ruled out at these more rigorous conditions. However, at the initial conditions of 300°/1350 atm, CS_2 was known not to decompose so it is ruled out in favor of the postulated adduct intermediate.

It is interesting to note that the ΔG_r at 800°K/1 atm for

$$CS_2 \rightarrow C + 2S \qquad (211)$$

is +3.9 Kcal[215]; yet under conditions of high pressure as much as 51% of the CS_2 did decompose. Since the reaction involves a loss of one mole of gaseous CS_2 the estimated contribution of -5 Kcal due to increased pressure[26] does allow this decomposition thermally.

An alternate decomposition of CS_2 to give CS and S which has been reported to occur at extreme temperatures does not appear to be thermodynamically feasible over the temperature range in this study. The reaction

$$CS_2 \rightarrow CS + S \qquad (212)$$

has a ΔG_r = +25.8 Kcal[215] at 600°K/1 atm and a ΔG_r = +26.0 Kcal[215] at 800°K/1 atm.

As was noted in the introduction CS_2 is known to form polymers like $(CS_2)_n$ and $(CS)_n$ at extreme pressures[29,108,199] but no such polymers were observed in this research.

5. The PF_3 - CO_2 System. The reaction between PF_3 and CO_2 had a higher temperature requirement for reaction than any of the previously discussed systems. The results of the PF_3 - CO_2 system are summarized in Tables XI and XX. It was observed that no reaction took place at conditions of 350°/4000 atm or 400°/670 atm. Reaction was first observed at 400°/1000 atm with 12% consumption of PF_3. The pressure dependence of this system is furthur shown at 400°/4000 atm where 41% of the PF_3 reacted. This initial reaction of PF_3 and CO_2 goes according to the equation

$$PF_3 + CO_2 \rightarrow OPF_3 + CO \qquad (213)$$

This reaction is only slightly favorable from an energetic viewpoint with a ΔG_r at 700°K/1 atm of -1.86 Kcal.[215] It is proposed that this reaction preceeds through an analogous pathway to those systems previously discussed with adduct formation followed by bond cleavage.

$$CO_2 + PF_3 \rightarrow O{=}C{=}\ddot{O}{:}\ddot{P}F_3 \qquad (214)$$

$$O{=}C{=}\ddot{O}{:}\ddot{P}F_3 \rightarrow C\ O + OPF_3 \qquad (215)$$

As can been seen the bond that must break from the intermediate adduct is a C=O bond. This bond energy is quite large (199.2 Kcal[217]) so this explains why such a larger temperature requirement is necessary.

As the temperature was increased to 500° a secondary reaction was noted.

$$PF_3 + CO \rightarrow OPF_3 + C \qquad (216)$$

This reaction did not occur at 400° as such a reaction was attempted with quantitative recovery of the starting materials at 400°/4000 atm.

Table XX

Reactions of PF_3 with CO_2

Pressure (atm)	Temperature (°C)	Conversion[a] (%)	Products
2670	300	-	-
335	350	-	-
4000	350	-	-
335	400	-	-
670	400	-	-
1000	400	12	OPF_3, CO
1350	400	11	OPF_3, CO
4000	400	41	OPF_3, CO
335	500	71	OPF_3, CO, C
4000	500	93	OPF_3, CO, C

[a] % of PF_3 consumed

At 500°/270 atm PF_3 and CO were found to react with 15% consumption of PF_3. The ΔG_r for this reaction at 800°K/1 atm is -9.2 Kcal[215] and and 700°K or about 400°C the ΔG_r is -13.5 Kcal.[215] The lack of reactivity of CO at 400° then appears to be due to the strong C O bond whose energy is 256.5 Kcal.[216] At 500° the proposed pathway is as follows

$$C\equiv O + \ddot{P}F_3 \rightarrow C\equiv O{:}\ddot{P}F_3 \qquad (217)$$

$$C\equiv O{:}\ddot{P}F_3 \rightarrow OPF_3 + C \qquad (218)$$

An alternate pathway which was ruled out would be the initial thermal decomposition of CO_2 via.

$$CO_2 \rightarrow CO + 1/2O_2 \qquad (219)$$

followed by the reaction of O_2 with PF_3

$$1/2O_2 + PF_3 \rightarrow OPF_3 \qquad (220)$$

This pathway was ruled out first of all because CO_2 was never observed to thermally decompose under the conditions employed in this research. It has been reported to undergo decomposition at 2800°K[156] which was far above the temperatures employed in this work. The actual reaction

$$CO_2 \rightarrow CO + 1/2O_2 \qquad (221)$$

would not be favored by high pressure and the ΔG_r for the reaction at 700°K/1 atm is +53.0 Kcal[215] and should be less spontaneous at higher pressures.

6. Summary of the Reactions of PF_3 with SO_2, H_2S, COS, CS_2 and COS. This series of reactions is related in that in each case PF_3 is acting as a Lewis acid in accepting an electron pair from the other molecule to form a proposed intermediate under high pressure. It is likely that PF_3 is assuming a petacoordinate, sp^3d, geometry for each of these intermediates. In each case a minimum temperature has been

reported where a secondary reaction, bond cleavage, is proposed to take place. Also, in each case a minimum pressure has been reported that is necessary for reaction to occur as well as somewhat lower pressures where no reaction was found to occur. From the experimental findings it appears that an order of base strength may be proposed, i.e., $SO_2 > H_2S > COS > CS_2 > CO_2$ towards bonding with PF_3. This series is based on the minimum temperature/pressure conditions for each reaction and for the most part is supported by the free energy calculations at minimum temperature for the initial reaction

$$AB + PF_3 \rightarrow A{-}B{:}PF_3 \rightarrow A + BPF_3$$

This trend is also supported by the order of the ease of breaking the A-B bond.

Table XXI summarizes the findings for this series of reactions.

Table XXI. Summary of Reactions of the Lewis Acid, PF_3, with a Series of Lewis Bases

Lewis Base	(°C) Minimum T For Reaction	(atm) Minimum P For Reaction	(atm) P at Minimum T For no Reaction	(Kcal) ΔG_r at Minimum T For Initial Reaction	(Kcal/mole) Bond Energy to Break A-B bond
SO_2	130	3000	2000	-50.9	34.9
H_2S	150	4000	2000	-28.5	82.9
COS	260	670	335	-30.4	76.9
CS_2	300	1350	1000	-10.8	131.7
CO_2	400	1000	670	- 1.9	199.2

CHAPTER IV

SUMMARY

A. This investigation was undertaken in order to study the high pressure effects on systems of small covalent molecules. The systems chosen for study were for the most part chemically unreactive at 1 atm up to temperatures of 500°. An important part of this study was to determine whether or not high pressure had any effect upon the reactions between these molecules. If a reaction was favored by elevated pressures the minimum conditions of both pressure and temperature were found. It was furthur determined how the reactions varied with conditions of pressure and temperature above the minimum requirements. The nature of these reactions, products formed as well as yields, was also determined. Finally, where possible, reaction pathways were postulated for these reactions, noting favorable pressure favored intermediates that would lead to the observed products.

B. Briefly summarized below are the experimental findings of this investigation.

1. The reaction between SF_6 and CS_2 was found not to occur at 485°/1000 atm. Reaction between SF_6 and CS_2 did occur at 485°/135 atm according to the equation

$$SF_6 + 2CS_2 \rightarrow (CF_3)_2S_2 + 3S \qquad (222)$$

At elevated temperatures of 520°/270 atm or 540°/4000 atm, the following reaction took place.

$$2SF_6 + CS_2 \rightarrow 2SF_6 + CF_4 + 2S \qquad (223)$$

2. No reaction occured between SF_6 and COS at 500°/170 atm; but at 500°/270 atm to 500°/4000 atm, SF_6 and COS reacted quantitatively according to the equation

$$SF_6 + COS \rightarrow SOF_2 + CF_4 \qquad (224)$$

3. Phosphorus trifluoride and CO_2 did not react at 400°/670 atm. At 400°/1000 atm reaction occured with 12% conversion of PF_3 which increased to 41% conversion of PF_3 at higher pressures according to the equation

$$PF_3 + CO \rightarrow OPF_3 + CO \qquad (225)$$

At higher temperatures the CO that formed reacted furthur with PF_3 with 93% conversion of PF_3 at 500°/4000 atm according to the equation

$$PF_3 + CO \rightarrow OPF_3 + C \qquad (226)$$

4. Phosphorus trifluoride and COS did not react below 260°/670 atm. At these conditions the following reactions did occur with 1% conversion of PF_3 which increased to 23% conversion of PF_3 at 300°/540 atm.

$$PF_3 + COS \rightarrow SPF_3 + CO \qquad (227)$$

At high pressures and temperatures of 300° to 400° a new reaction was noted. (300°/3000 atm to 400°/4000 atm)

$$3PF_3 + 3COS \rightarrow SPF_3 + 2OPF_3 + CO + CS_2 + C \qquad (228)$$

5. No reaction occured between PF_3 and CS_2 at 300°/1000 atm. From 300°/1350 atm to 500°/4000 atm the following reaction did occur with conversions of PF_3 of from 4% to 70% respectively.

$$2PF_3 + CS_2 \rightarrow 2SPF_3 + C \qquad (229)$$

6. Phosphorus trifluoride and H_2S did not react at 150°/4000 atm or 200°/135 atm but 3% of PF_3 reacted at 15°/4000 atm or 200°/1350 atm with a maximum conversion of 48% of PF_3 at 300°/280 atm according to the equation

$$PF_3 + H_2S \rightarrow SPF_3 + H_2 \tag{230}$$

7. No reaction between PF_3 and SO_2 was found to occur at 150°/335 atm or 130°/2000 atm. At 130°/3000 atm 14% of the PF_3 was consumed and at 150°/670 atm 4% of PF_3 was consumed with a maximum of 95% PF_3 consumption at 500°/4000 atm. In all cases the reaction was

$$2PF_3 + SO_2 \rightarrow 2OPF_3 + S \tag{231}$$

8. Phosphorus trifluoride and SF_6 did not react at 450°/335 atm. At 485°/4000 atm the following reaction did occur.

$$3PF_3 + SF_6 \rightarrow 3PF_5 + S \tag{232}$$

At less vigorous conditions, 485°/335 atm and 450°/4000 atm another unique reaction took place

$$PF_3 + SF_6 \rightarrow PF_5 + SF_4 \tag{233}$$

or

$$S + 2PF_5 \rightarrow SF_4 + 2PF_3 \tag{234}$$

9. A reaction took place between SF_6, CO and S at 500°/4000 atm according to the equation

$$SF_6 + 5CO + S \rightarrow 3COF_2 + 2COS \tag{235}$$

10. Sulfonyl fluoride was found to react with CS_2 at 500°/4000 atm according to the equation

$$5SOF_2 + 8CS_2 \rightarrow (CF_3)_2S + 5COS + CF_4 + 15S \tag{236}$$

11. Thiophosphoryl fluoride and SO_2 did not react at 170° under autogenous pressure in a glass reactor but did react at 130°/4000 atm and 150°/4000 atm to give over 70% conversion of SPF_3

according to the equation

$$2SPF_3 + SO_2 \rightarrow 2OPF_3 + 3S \qquad (237)$$

12. Carbon disulfide was found to decompose at 500°/270 atm (51% decomposition) and 500°/4000 atm (40% decomposition) according to the equation

$$CS_2 \rightarrow C + 2S \qquad (238)$$

13. Carbon was found to react with SF_6 at 500°/4000 atm with 47% of the SF_6 consumed according to the equation

$$C + 2SF_6 \rightarrow CF_4 + 2SF_4 \qquad (239)$$

14. Bisperfluoromethyl disulfide decomposed to the monosulfide (91% decomposition) at 500°/50 atm according to the equation

$$(CF_3)_2S_2 \rightarrow (CF_3)_2S + S \qquad (240)$$

15. Bisperfluoromethyl disulfide reacted with SF_6 at 540°/4000 atm according to the equation

$$(CF_3)_2S_2 + 5SF_6 \rightarrow 2CF_4 + 7SF_4 \qquad (241)$$

16. Bisperfluoromethyl disulfide reacted with CS_2 at 540°/4000 atm to give a mixture of perfluoroalkanes, carbon and sulfur according to the equation

$$(CF_3)_2S_2 + CS_2 \rightarrow C_nF_{2n+2} + C + S \qquad (242)$$

$$(n = 1 \text{ to } 5)$$

17. The following group of compounds were found not to react at conditions up to 500°/4000 atm.

$SF_6 + CO_2 \rightarrow$ no reaction

$SF_6 + CO_2 \rightarrow$ no reaction

$COS \rightarrow$ no reaction

$CS_2 + COS \rightarrow$ no reaction

$CS_2 + CO_2 \rightarrow$ no reaction

$CS_2 + CF_4 \rightarrow$ no reaction (248)

$C + CF_4 \rightarrow$ no reaction (249)

$S + CF_4 \rightarrow$ no reaction (250)

$S + SF_6 \rightarrow$ no reaction (251)

Appendix I

The figure below is a schematic diagram of the high pressure-high vacuum system designed by J. J. Moscony, R. I. Harker, and A. G. MacDiarmid.[140]

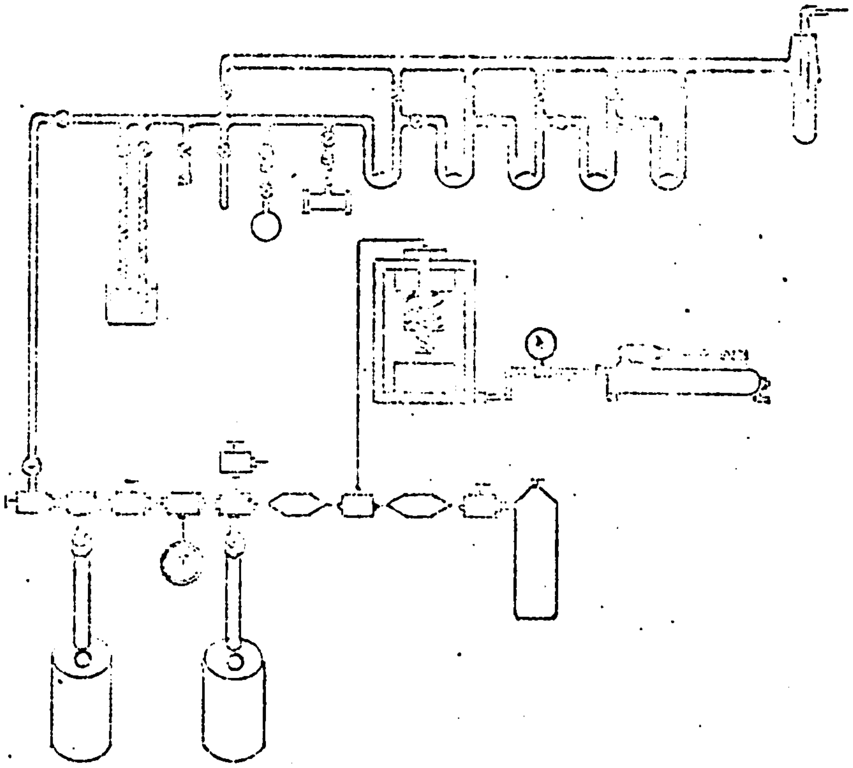


Figure 5 Diagram of High-Pressure System

Appendix II

Summary of Some Preliminary Studies into Other High Pressure Systems Not Reported in this Dissertation

A. The PF_3 and SiO_2 System

PF_3 and SiO_2 were found to react at a variety of pressures and temperatures. The products were identified by infrared and mass spectroscopy. A trace of SiF_4 was found from a reaction mixture at 4000 atm and 25°. At 200° and 670 atm, more SiF_4 was observed but no other product was identified. At 280° and 4200 atm $(SiF_3)_2O$ and SiF_4 were identified. The reaction of PF_3 and SiO_2 at 3600 atm and 500° gave $(SiF_3)_2O$, SiF_4 and OPF_3 as products.

For those conditions of 200° or below and at pressures of 670 to 4000 atm the following reaction may be postulated:

$$4PF_3 + 3SiO_2 \rightarrow 3SiF_4 + P_2O_3{}^{19} \qquad (252)$$

At 280° and 4000 atm the reaction between SiF_4 and SiO_2 as reported by Moscony[140] is occuring viz

$$3SiF_4 + SiO_2 \rightarrow 2(SiF_3)_2O \qquad (253)$$

The reaction at 3600 atm and 500° probably occurs as follows:

$$2PF_3 + SiO_2 \rightarrow 2OPF_3 + Si \qquad (254)$$

B. The PF_3 and NH_3 System

The reaction between PF_3 and NH_3 took place at 2800 atm and at temperatures of 200° and 500°. In both cases NH_4F was identified from infrared and mass spectra to be one of the products formed. No volatile compounds were formed in either reaction; however, in the reaction at 200°, a red brown solid was observed in the gold tube.

C. The PF_3 and CH_4 System

It was found that SiF_4 and SO_2 did not react at conditions of 2650 atm and 300° or at 3333 atm and 500°. The reactant gases were recovered quantatively and identified from the infrared spectrum.

I. The SiF_4 and Mg_3N_2 System

There was no reaction between SiF_4 and Mg_3N_2 at 4000 atm and 280° but at 3467 atm and 500°, a new solid was observed mixed with the Mg_3N_2. This solid was not identified.

J. The SiF_4 and PF_3 System

It was found that SiF_4 and PF_3 did not react under any conditions of pressure and temperature up to 4267 atm and 500°. The reactants were recovered quantitatively and identified by infrared spectrum.

K. The SiF_4 and SF_6 System

SiF_4 and SF_6 did not react at conditions of 4000 atm at 280° or 3600 atm at 500°. The reactants were recovered quantitatively and identified by infrared spectrum.

L. The SiF_4 and CO_2 System

There was no reaction between SiF_4 and CO_2 at either 3933 atm and 280° or 3467 atm and 500°. The reactants were recovered quantitively and identified by infrared spectrum.

M. The CF_4 and SiO_2 System

CF_4 and SiO_2 did not react at 4533 atm and at temperatures from 280° to 500°. The CF_4 was always recovered quantitatively and identified by infrared spectrum.

N. The CF_4 and CO_2 System

No reaction was observed between CF_4 and CO_2 at 280° and 4000 atm. The reactant gases were recovered quantitatively and identified by infrared spectrum.

O. The CF_4 and SF_6 System

No reaction occured between CF_4 and SF_6 at 280° and 4000 atm. The reactant gases were recovered quantitatively and identified by the infrared spectrum.

BIBLIOGRAPHY

1. E. W. Able, R. Hoenigschmid-Grossech and S. M. Illingsworth, J. Chem. Soc., (A), 2623 (1968).
2. I. S. Akhmetzhanov, Zh. Obshch. Khim., 38, 1090 (1968) CA:69:66829h.
3. N. F. Albertson and W. C. Fernelius, J. Amer. Chem. Soc, 65, 1687 (1943).
4. H. C. Allen and E. K. Plyler, J. Chem. Phys., 25, 1132 (1956).
5. E. R. Alton and J. C. Carter, U.S. Dept. Commerce, Office of Tech. Ser., P. B. Report No. 161, 080 (1959).
6. E. R. Alton, Dissertation Abstracts, 21, 3620 (1961)
7. American Petroleum Institute Research Project 44, Spectra No. 196, 401, 444, 445, 729.
8. F. Applegath and R. A. Rranz, U.S. Patent 2 002 896, Jul. 18, 1961.
9. A. J. Arvia and P. J. Aymonino, Spectrochim. Acta., 18, 1299 (1962).
10. A. V. Avdeeva, J. Chem. Ind. (U.S.S.R.), 14, 1077 (1937) CA:32:734^9.
11. E. E. Aynsley, R. Nichols and P. L. Robinson, J. Chem. Soc., 623 (1953).
12. L. Barton, J. Inorg. Nucl. Chem., 30, 1683 (1968).
13. M. Baudler, H. W. Valpertz and K. Kipker, Chem. Ber., 100, 1766 (1967).
14. M. Becke-Goehring and W. Lehr, Chem. Ber., 94, 1591 (1961)
15. F. Beguin and R. Setton, Bull. Soc. Chim. Fr., 11, 3814 (1970).
16. M. Bigorgne and A. Zelwer, Bull. Soc. Chim. Fr., 1986 (1960).
17. L. P. Blanchard and P. LeGoff, Can. J. Chem., 35, 89 (1957).

18. A. J. Bloodworth, A. G. Davies and S. C. Vasishtha, J. Chem. Soc., (C), 1309 (1967).

19. H. S. Booth and A. R. Bozarth, J. Amer. Chem. Soc., 61, 2927 (1939).

20. H. S. Booth and B. B. Dutton, J. Amer. Chem. Soc., 61 2937 (1939).

21. H. S. Booth and C. A. Seabright, J. Amer. Chem. Soc., 65, 1834 (1943).

22. H. S. Booth and C. F. Swinehart, J. Amer. Chem. Soc., 54, 4751 (1932).

23. H. S. Booth and J. H. Walkup, J. Amer. Chem. Soc., 65, 2334 (1943).

24. J. Bouix and R. Hillel, Can. J. Chem., 51, 292 (1973).

25. H. J. M. Bowen, Trans. Faraday Soc., 50, 452 (1954).

26. R. S. Bradley and D. C. Munro, High Pressure Chemistry, Permagon Press, Oxfor, 1965.

27. G. A. R. Brandt, H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 2198 (1952).

28. G. A. R. Brandt, H. J. Emeléus and R. N. Hazeldine, J. Chem. Soc., 2549 (1952).

29. P. W. Bridgman, Proc. Am Acad. Arts Sci., 74, 399 (1941).

30. F. E. Brown and F. A.Griffiths, Iowa State Col. J. of Sci., 9, 89 (1934) CA:29:5333^3.

31. M. Brownstein and R. J. Gillespie, J. Amer. Chem. Soc,. 92, 2718 (1970).

32. A. B. Burg, J. Amer. Chem. Soc., 65, 1929 (1943).

33. H. J. Callomon, D. C. McKean and H. W. Thompson, Proc. Roy. Soc. (london), A208, 341 (1951).

34. H. A. Carter, C. S-C. Wang and J. M. Shreeve, Spectrochim. Acta., 29, 1479 (1973).

35. J. R. Case and F. Nyman, Nature, 193, 473 (1962).

36. J. R. Case and H. L. Roberts, Inorg. Chem., 5, 333 (1966).

37. R. L. Cauble and G. H. Cady, J. Amer. Chem. Soc., 89, 1962 (1967).

38. R. G. Cavell, can. J. Chem., 46, 613 (1968).

39. R. G. Cavell, Spectrochim. Acta., **23**, 249 (1967)

40. J. H Centerford and T. A. O'Donnel, Inorg. Chem., **5**, 1442 (1966).

41. M. Chaigneau and M. Santarromana, C. R. Acad. Sci. Ser. C., **269**, 1643 (1969).

42. L. Coes, *Modern Very High Pressure Techniques*, R. H. Wentorf, ed., Butterworths, Washington, D.C., 1962.

43. D. Costeanu, Compt. Rend., **157**, 934 (1914).

44. J. D. Cotton and T. C. Waddington, J. Chem. Soc. (A) , 793 (1966).

45. H. C. Cowen, F. Riding and E. Warhurst, J. Chem. Soc., 4168 (1953).

46. P. A. W. Dean and D. G. Ibbot, Inorg. Nucl. Chem. Lett., **11**, 119 (1975).

47. R. E. A. Dear and E. E. Gilbert, J. Fluorine Chem., **4**, 107 (1974).

48. L. Delachaux, Helv. Chim. Acta., **10**, 195 (1927).

49. G. C. Demitras and A. G. MacDiarmid, Inorg. Chem., **3** 1198 (1964).

50. P. Drude and W. Nernst, Z. Physik. Chem. (Leipzig), **15**, 79 (1894).

51. R. E. Dodd, L. A. Woodward and H. L. Roberts, Trans. Faraday Soc., **52**, 1052 (1956).

52. F. Ebel and E. Bretscher, Helv. Chim. Acta., **12**, 450 (1929).

53. E. A. V. Ebsworth, G. Rocktaschel and J. C. Thompson, J. Chem. Soc,. **(A)**, 362 (1967).

54. C. A. Eckert, *Ann. Rev. Phys. Chem.*, **23**, 239 (1972).

55. D. A. Edwards and R. T. Ward, Inorg. Nucl. Chem. Lett., **9**, 145 (1973).

56. F. W. Einstein, E. Enwall, N. Flitcroft and J. M. Leach, J. Inorg. Nucl. Chem., **34**, 885 (1972).

57. A. J. Ellis, J. Chem. Soc., 3689 (1959).

58. A. J. Ellis and D. W. Anderson, J. Chem. Soc., 1765 (1961).

59. A. J. Ellis and D. W. Anderson, J. Chem. Soc., 4678 (1961).

60. A. J. Ellis and W. S. Fyfe, Rev. Pure and Appl. Chem. (Australia), **7**, 261 (1957).

61. H. J. Emeléus and K. J. Packer, J. Chem Soc., 771 (1962).

62. A. H. Ewald, Discussions Faraday Soc., 22, 138 (1956).

63. A. H. Ewald, S. D. Hamann and J. E. Stutchbury, Trans. Faraday Soc., 53, 991 (1957).

64. T. P. Fehlner and S. A. Fridmann, J. Phys. Chem., 75, 2711 (1971).

65. R. J. Ferm, Chem. Revs., 57, 621 (1957).

66. E. Fluck and H. Binder, Angew. Chem., 77, 381 (1965).

67. C. E. Frank, A. T. Hallowell, C. W. Theobald and G. T. Vaala, Ind. Eng. Chem., 41, 2061 (1949).

68. H. H. Franck and B. Meppin, Z. Angew. Chem., 43, 726 (1930).

69. W. W. Gleave, U.S. Patent 2104695, Jan. 4, 1937.

70. P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc., 57, 1877 (1961).

71. M. G. Gonikberg, V. M. Zhulin and B. S. El'yanov, The Physics and Chemistry of High Pressures, Olympia Symposium, Goorden and Breach, eds., New York, 1963, p. 212.

72. J. Goubeau. W. Bues and F. W. Kampmann, Z. Anorg. Allg. Chem., 283, 123 (1956).

73. A. Granger, C. R. Acad. Sci., Paris, 120, 923 (1895).

74. A. Granger. C. R. Acad. Sci., Paris, 123, 176 (1896).

75. A. Granger, Bull. Soc. Chim, Paris [3], 13, 873 (1895).

76. J. E. Griffiths and A. B. Burg, J. Amer. Chem. Soc., 82, 1507 (1960).

77. J. E. Griffiths and A. B. Burg, J. Amer. Chem. Soc., 84, 2309 (1962).

78. A. Guntz, C. R. Acad. Sci., Paris, 103, 58 (1886).

79. H. S. Gutowsky and A. D. Liehr, J. Chem. Phys., 20, 1652 (1952).

80. A. P. Hagen, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania.

81. A. P. Hagen and E. A. Elphingstone, Inorg. Chem., 12, 478 (1973).

82. A. P. Hagen and E. A. Elphingstone, J. Inorg. Nucl. Chem., 35, 3719 (1973).

83. A. P. Hagen and E. A. Elphingstone, J. Inorg. Nucl. Chem., 36, 509 (1974).

84. A. P. Hagen and E. A. Elphingstone, Syn. Inorg. Metal-Org. Chem., 2, 335 (1972).

85. A. P. Hagen D. J. Jones and S. R. Ruttman, J. Inorg. Nucl. Chem., 36, 1217 (1974).

86. A. P. Hagen and A. G. MacDiarmid, Inorg. Nucl. Chem. Lett., 6, 413 (1970).

87. S. D. Hamann, High Pressure Physics and Chemistry, R. S. Bradley, ed., Academic Press, Inc., London, 1968, 2, Chapt. 8, p. 163.

88. S. D. Hamann, Physico-Chemical Effects of Pressure, Academic Press, Inc., New York, 1957.

89. S. D. Hamann, Trans. Faraday Soc., 54, 507 (1958).

90. R. J. Harder and W. C. Smith, J. Amer. Chem. Soc., 83, 3422 (1961).

91. A. P. Harris and K. E. Weale, J. Chem. Soc., 146 (1961).

92. O. Hartmanshenn and J. C. Barral, C. R. Acad. Sci., SerC., 272, 2139 (1971).

93. W. R. Hasek, W. C. Smith and V. A. Engelhardt, J. Amer. Chem. Soc., 82, 543 (1960).

94. R. N. Hazeldine and J. M. Kidd, J. Chem. Soc., 3219 (1953).

95. R. N. Haszeldine and J. M. Kidd, J. Chem. Soc., 3871 (1955).

96. G. B. Heisig and O. C. Frykholm, Inorganic Synthesis, I, H. S. Booth, ed., McGrew Hill Book Co., New York, 1939, p. 157.

97. L. G. Hepler, J. Phys. Chem., 69, 965 (1965).

98. D. L. Hildenbrand, Chem. Phys. Lett., 15, 379 (1972).

99. D. L. Hildenbrand, J. Phys. Chem., 77, 897 (1973).

100. F. A. Hohorst and J. M. Shreeve, J. Amer. Chem. Soc., 89, 1809 (1967).

101. R. R. Holmes and R. P. Wayner, Inorg. Chem., 2, 384 (1963).

102. G. R. Hunt and M. K. Wilson, Spectrochim Acta., 16, 570 (1960).

103. H. F. Johnstone, Ind. Eng. Chem., 34, 1017 (1942).

104. W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Prentice Hall Inc., New Jersy, 1970.

105. E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielsen, J. Chem. Phys., 19, 242 (1951).

106. R. E. Kirk and D. F. Othmer, eds, Encylopedia of Chemical Technology, 3, The Interscience Encylcopedia, Inc., New York, 1949, p. 142.

107. R. W. Kiser, J. G. Dillard and D. L. Dugger, Advan. Cehm. Ser., No 72, 153 (1968).

108. K. J. Klabunde, C. M. White and H. F. Efner, Inorg. Chem., 13, 1778 (1974).

109. R. Klein, A. Bliss, L. Schoen and H. G. Nadeau, J. Amer. Chem. Soc., 83, 4131 (1961).

110. G. Kodama and R. W. Parry, Inorg. Chem., 4, 410 (1965).

111. G. Kodama and R. W. Parry, J. Inorg. Nucl. Chem., 17, 125 (1961)

112. L. Kolditz, Z. Anorg. U. Allgem. Chem., 280, 313 (1955).

113. T. N. Komarova and V. P. Kindoeva, Issled. Obl. Neorg. Tekhnol., 341 (1972) CA:77:1314513S.

114. T. Kruck, Z. Naturforsch, 196, 165 (1964).

115. T. Kruck and K. Baur, Chem. Ber., 98, 3070 (1965).

116. R. T. Lagemann and E. A. Jones, J. Chem. Phys., 19, 534 (1951).

117. E. W. Lawless and L. D. Harman, J. Inorg. Nucl. Chem., 31, 1541 (1969).

118. W. J. leNoble, J. Amer. Chem. Soc., 82, 5253 (1960).

119. W. J. LeNoble, Progress in Physical Organic Chemistry, 5 A. Stritwieser and R. W. Taft, eds., Interscience Publishers, New York, 1967, p. 207.

120. S-C Li, J. Chinese Chem. Soc, 11, 14 (1944) CA:39:1099^2

121. A. Lord and H. O. Pritchard, J. Chem. Thermodyn., 1, 495 (1969).

122. W. Ludovici, Ger. Offen. 2131030, Dec. 28, 1972.

123. M. Lustig and J. K. Ruff, Inorg. Chem., 6, 2115 (1967).

124. M. Lustig, Inorg. Chem., 4, 104 (1965).

125. H. N. Madon and R. F. Strickland-Constable, Ind. Eng. Chem., 50, 1189 (1958).

126. E. H. Man, D. D. Coffman and E. L. Muetterties, J. Amer. Chem. Soc., 81, 3575 (1959).

127. B. Meyer, T. V. Oommen, B. Gotthardt and T. R. Hooper, Inorg. Chem., 10, 1632 (1970).

128. R. Meyer and S. Schuster, Ber., 44, 1931 (1911).

129. C. C. McCune, F. W. Cagle, Jr and S. S. Kistler, J. Phys. Chem., 64, 1773 (1960).

130. D. H. McDaniel and W. G. Evans, Inorg. Chem., 5, 2180 (1966).

131. D. R. McKelvey and K. R. Brower, J. Phys. Chem., 64, 1958 (1960).

132. H. Moissan, C. R. Acad. Sci., Paris, 99, 655 (1884).

133. H. Moissan, Ann, Chim. Phys. [6], 6, 433 (1885).

134. H. Moissan, C. R. Acad. Sci, Paris, 99, 970 (1884).

135. H. Moissan, C. R. Acad. Sci., Paris, 100, 1348 (1885).

136. H. Moissan, C. R. Acad. Sci., Paris, 102, 1245 (1886).

137. H. Moissan, Ann. Chim. Phys. [6], 19, 286 (1890).

138. H. Moissan, Bull. Soc. Chim. Fr. 3, 4, 260 (1890).

139. E. Montignie, Bull. Soc. Chim. Fr., 8, 198 (1941).

140. J. J. Moscony, R. I. Harker and A. G. MacDiarmid, Rev. Sci. Inst., 38, 138 (1967).

141. A. Mueller and R. Menge, Z. Anorg. Allgem. Chem., 393, 259 (1972).

142. E. L. Muetterties, Advances in Stereochemistry of Coordination Compounds, 509 (1962).

143. E. L. Muetterties, T. A. Bither, M. W. Farlow and D. D. Coffman, J. Inorg. Nucl. Chem., 16, 52 (1960).

144. E. L. Muetterties, D. D. Coffman and C. W. Tullock, J. Amer. Chem. Soc., 86, 357 (1964).

145. E. L. Muetterties, H. L. Jackson and F. D. March, Inorg. Chem., 2, 43 (1963).

146. S. Nagase, H. Baba, K. Kodaiva and T. Abe, Bull. Chem. Soc. Japan, 46, 3435 (1973).

147. S. Nakamura and M. Ito, U.S. Patent 3652203, Mar. 28, 1972.

148. G. Neumann and W. Neumann, J. Organometal. Chem., 42, 293 (1972).

149. R. C. Neumann, Jr., Accounts of Chemical Research, 5, 381 (1972).

150. R. C. Neuman, Fr. and R. P. Pankratz, J. Amer. Chem. Soc., 95, 8372 (1973).

151. A. E. Nicholson and R. G. W. Norrish, Discussions Faraday Soc., 22, 97 (1956).

152. A. H. Ni-lsen, T. G. Burke, P. J. H. Woltz and E. A. Jones, J. Chem. Phys., 20, 596 (1952).

153. T. H. Norris and E. J. Woodhouse, Inorg. Chem., 10, 614 (1971).

154. T. A. O'Donnell and D. F. Stewart, Inorg. Chem., 5 1434 (1966).

155. J. K. O'Loane and M. K Wilson, J. Chem. Phys., 23, 1313 (1955).

156. H. W. Olschewski, J. Troe and H. G. Wagner, Ber. Bunsengers, Phys. Chem., 70, 1060 (1966).

157. A. A. Opalòvskii and E. U. Lobkov, J. Fluorine Chem., 2, 349 (1972-73).

158. A. A. Opalovskii, E. U. Lobkov, B. G. Erenburg, Yu. V. Zakhar'ev and V. G. Shingarev, Izv. Akad. Nauk. U.S.S.R. Neorg. Mater., 8, 1877 (1972).

159. A. L. Oppegard, W. C. Smith, E. L. Muetterties and V. A. Engelhardt, J. Amer. Chem. Soc., 82, 3835 (1960).

160. D. K. Padma, A. R. Vasudeva Murthy, W. Becher and J. Massonne, J. Fluorine Chem., 2, 113 (1972-73).

161. D. K. Padma and A. R. Vasudeva Murthy, Inorg. Chem., 3, 1653 (1964).

162. R. W. Parry and T. C. Bissot, J. Amer. Chem. Soc., 78, 1524 (1956).

163. R. W. Parry and T. C. Bissot, W.A.D.C. Tech. Report 56-318; A.S.T.I.A Document No. A.D. 97233 (Aug., 1956).

164. J. R. Partington and H. H. Neville, J. Chem. Soc., 1230 (1951).

165. G. Pass and H. L. Roberts, Inorg. Chem., 2, 1016 (1963).

166. T. C. Peng, J. Phys. Chem., 78, 634 (1974).

167. E. Philippot and M. Conte, C. R. Acad. Sci., Paris, Ser C, 267, 1813 (1968).

168. N. V. Philips' Gloeilampenfrabrieken, Neth. Appl. 6915057, Apr. 6, 1971. CA:75:68219g.

169. R. H. Pierson, A. N. Fletcher and E. St. C. Gantz, Anal. Chem., 28, 1218 (1956).

170. A. M. Polyakova, V. V. Korshak and A. A. Shakharova, Isvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk, 979 (1956) CA:51:4979b.

171. C. Poulenc, C. R. Acad. Sci., Paris, 113, 75 (1891).

172. M. Prince and J. Hornyak, Chem. Commun., 455 (1966).

173. H. W. Roesky, O. Glemser and D. Bormann, Chem. Ber., 99, 1589 (1966).

174. F. E. Saalfeld and M. V. McDowell, (U.S.) Naval Res. Lab. Report 6639, 1967.

175. D. T. Sauer and J. M. Shreeve, Inorg. Chem., 9, 2797 (1970).

176. C. J. Schack and R. D. Wilson, Inorg. Chem., 9, 311 (1970).

177. M. Schmidt and D. Eichelsdoerfer, Z. Anorg. Allgem. Chem., 330, 130 (1964).

178. H. Schulze, Bull. Soc. Chim. Fr., 35, 173 (1881).

179. A. S. Selivanova and Ya. K. Syrkin, Acta. Physicochim. U.R.S.S., 11, 647 (1939) CA:343160^2

180. B. Siegel and P. Breisacher, J. Inorg. Nucl. Chem., 31, 675 (1969).

181. B. Siegel and P. Breisacher, J. Inorg. Nucl. Chem., 32, 1469 (1970).

182. A. R. Shah, D. K. Padma and A. R. Vasudeva Murthy, Indian J. Chem., 9, 885 (1971).

183. K. G. Sharp and J. L. Margrave, Inorg. Chem., 8, 2655 (1969).

184. R. D. Shelton, A. H. Nielsen and W. H. Fletcher, J. Chem. Phys., 21, 2178 (1953).

185. J. M. Shreeve and G. cady, J. Amer. Chem. Soc., 83, 4521 (1961).

186. E. Sinn, Coor. Chem. Rev., 12, 185 (1974).

187. P. Silber. E. Philippot and M. Maurin, Comp. Rend., 261, 4126 (1965).

188. E. A. Smirnov, B. A. Knyazev, V. A. Petrunin and Yu. M. Zinov'ev, Zh. Neorg. Khim., 14, 847 (1969) CA:70:102639e.

189. W. C. Smith and V. A. Englehardt, J. Amer. Chem. Soc., 82, 3838 (1960).

190. B. C. Smith and G. H. Smith, J. Chem. Soc., 5516 (1965).

191. A. G. Streng, J. Amer. Chem. Soc., 85, 1380 (1963).

192. R. Steudel, Z. Anorg. Allgem. Chem., 346, 255 (1966).

193. M. F. Taradoire, 14 me Congr. Chim. Ind, Paris, Oct. 1934. CA:29:6710^{4}.

194. G. Tarbutton, E. P, Egan Jr. and E. P. Frary, J. Amer. Chem. Soc., 63, 1782 (1941).

195. B. W. Tattershall and G. H. Cady, J. Inorg. Nucl. Chem., 29, 3003 (1967).

196. E. Terres and H. Wesemann, Z. Angew. Chem., 45, 795 (1932).

197. T. E. Thorpe and J. W. Rodger, J. Chem. Soc., 53, 766 (1888).

198. L. E. Trevorrow, J. Fischer and W. H. Gunther, Inorg. Chem., 2, 1281 (1963).

199. H. S. Turner, Chem. in Britain, 4, 245 (1968).

200. M. E. Vol'pin and I. S. Kolomnikov, Pure Appl. Chem., 33, 567 (1973).

201. C. Walling and M. Naiman, J. Amer. Chem. Soc., 84, 2628 (1962).

202. C. Walling and H. J. Schugar, J. Amer. Chem. Soc., 85, 607 (1963).

203. U. Wannagat and J. Rademachers, Z. Anorg. U. Allgem. Chem., 289, 66 (1957).

204. T. Wartik and E. F. Apple, J. Amer. Chem. Soc., 80, 6155 (1958).

205. T. Wartik and R. K. Pearson, J. Inorg. Nucl. Chem., 7, 404 (1958).

206. T. Wentink, J. Chem. Phys., 29, 188 (1958).

207. E. Whalley, Annu. Rev. Phys. Chem., 18, 205 (1967)

208. E. Whalley, Can. J. Chem., 38, 2105 (1960).

209. J. N. Wilson, J. Amer. Chem Soc., 80, 1338 (1958).

210. R. L. Wilkens, J. Chem. Phys., 51, 853 (1969).

211. A. A. Woolf, J. Chem. Soc., 1053 (1950).

212. A. A. Woolf, J. Chem. Soc., 279 (1955).

213. V. M. Zhulin, M. G. Gonikberg and R. I. Baikova, Bull. Akad Sci. U.S.S.R., Div. Chem. Sci. (Eng. Trans.), 418 (1965).

215. JANAF Thermochemical Tables, U.S. Dept. Commerce, National Bureau of Standards, Institute For Applied Technology, 1961. and First Addendum, 1966.

216. F. A. Cotton and G. Wilkinson, <u>Advanced Inorganic Chemistry 3 ed.</u>, John Wiley and Sons, New York, 1972.

217. F. Ebel and E. Bretscher, Helv. Chim. Acta, <u>12</u>, 443 (1929).